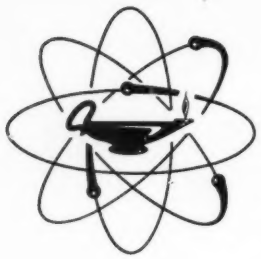
1971
Quarterly
Technical
Progress
Review
Volume 8-3

Isotopes & Radiation Technology

Prepared for
Division of
Technical
Information –
Division of
Isotopes
Development
U.S. Atomic Energy Commission
by Isotopes
Information
Center
Oak Ridge
National Laboratory

XUM



ISOTOPES INFORMATION CENTER

for ISOTOPES INFORMATION

THE ISOTOPES INFORMATION CENTER IS SUPPORTED BY THE U. S. ATOMIC ENERGY COMMISSION, DIVISION OF ISOTOPES DEVELOPMENT

IIC collects worldwide information on production and uses of radioisotopes.

IIC information covers such areas as

- Preparation of Radioisotopes and Enrichment of Stable Isotopes
- Radioactive or Stable Isotope Targets
- Radioisotope or Machine Irradiators for Large-Scale Irradiations, both Industrial and Research
- Radioisotopes as Energy Sources
- Radioisotopes in Industry and Other Areas of Technology
- Radioisotopes in Physical Sciences
- Radioisotopes in Life Sciences
- Safety with Radioisotopes

IIC publishes bibliographies, compilations, and state-of-the-art reviews on in-scope areas.

IIC will provide information to help you in solving your research and production problems.

Direct all inquiries to:

P. S. Baker, Director
Isotopes Information Center
Oak Ridge National Laboratory
Post Office Box X
Oak Ridge, Tennessee 37830
Telephone 615-483-8611, Ext. 3-1742
FTS number is 615-483-1742

ISOTOPES
INFORMATION
CENTER

COVER: The first pure californium, magnified about 90 times, which was isolated in 1960. The californium was in the form of the isotope ^{249}Cf. The crystals are lodged in a capillary tube. (Photograph is from the University of California, Berkeley, Lawrence Radiation Laboratory.)

XUN

Isotopes and Radiation Technology

Vol. 8, No. 3 Spring 1971

Contents

I Isotope Production and Development

253 **Fission-Product Xenon and Krypton—An Opportunity for Large-Scale Utilization** *C. A. Rohrmann*
255 Discussion
259 Cost, Value, and Price
260 **^{90}Sr Heat Sources** *Roberta Shor, R. H. Lafferty, Jr., and P. S. Baker*
261 Selection of ^{90}Sr as Heat Source
264 Operation of Radioisotope-Powered Electric Generators
264 Separation Processes
268 Preparation of Strontium Titanate
272 Fuel Fabrication
276 Source Encapsulation and Testing
280 Examination of Used Sources
283 Properties of Strontium Fuel Forms

II Isotope Technology Development

287 **Flow Measurements with Radioisotopes** *R. H. Lafferty, Jr.*
287 Survey of Flow-Measurement Techniques
291 Radioactive-Tracer Measurements
292 Accuracy and Precision
294 Choice of Radioactive Tracer
297 Injection of Tracer
302 Gas-Flow Measurements by Induced Ionization
304 Nontracer Uses of Radioisotopes for Flow Measurements
307 Applications of Radioisotope Flow Measurements
309 **The Application of Nuclear Techniques to the Recovery of Faded Photographs** *R. M. Chatters and Camille Jacobs*
310 Long-Exposure Method
315 **Labeling of Copper Wire with ^{110m}Ag for Subsequent Identification** *L. C. Bate and F. F. Dyer*
315 Procedure
316 Results
317 Safety
317 **Radioisotopic X-Ray Gage for Determining Particle-Size Distribution**
318 **A Simple Neutron Radiography Set**
319 **^{13}C Helps Reveal Carbohydrate Structure**
320 *The Carbon-14 Dating of Iron*
320 *Radiography Using Photo-Nuclear Reaction*

XUM

III Food Irradiation

321 **Study of Irradiated Pasteurized Fishery Products** *L. J. Ronsivalli, F. J. King, V. G. Ampola, and J. A. Holston*
321 Results of the Past Work
322 Maximum-Shelf-Life Study
323 Radiation Effects on Chemical Composition of Cod and Haddock
333 General Discussion

IV Isotopic Heat and Power Development

341 **ORNL Isotope Kilowatt Program** *A. P. Fraas*
341 Organic Rankine-Cycle System
344 Steam Rankine-Cycle System
345 Thermoelectric System

V Applications in Life Sciences

346 **Dual Radioisotopic Method for Diagnosis of Pulmonary Embolism**
347 **Radioisotopes and Rice**
348 **Frostbite Evaluation with ^{131}I-RISA**
348 **Neutrons from ^{2}H and ^{3}H May Fight Cancer**
349 *Molecular Radiation Biology* **(Book Review)**
349 *Radiation Sensitivity of Toxins and Animal Poisons* **(Book Review)**
349 *Medical Radionuclides: Radiation Dose and Effects* **(Book Review)**

VI Safety

350 **Shipping-Cask Evaluation** *R. D. Seagren*
350 Regulatory Requirements
353 Developments
354 Design
356 Fabrication
357 Testing
359 Approval

VII Isotopes Around the World

360 **Developments Abroad on Radioisotope-Powered Cardiac Pacemakers** *Martha Gerrard*
360 France
361 United Kingdom
361 Australia
362 Switzerland
362 Safety
363 **Isotope Group of Sweden Celebrates 10 years of Operation**

VIII Miscellaneous

364 **Availability of Isotopes and Services**
366 **AEC Activities**
368 **General**

Superintendent of Documents, U. S. Government Printing Office, Washington, D. C. 20402, $2.50 per year.

XUM

Isotopes and Radiation Technology

is a Technical Progress Review prepared by the Isotopes Information Center, Oak Ridge National Laboratory, at the request of the Divisions of Technical Information and Isotopes Development, U. S. Atomic Energy Commission. This Review is intended to assist those interested in keeping abreast of significant developments in the fields of isotopes and radiation technology. It is not a comprehensive review of all literature published in this field during a given quarter; rather, it is a mechanism for presenting concise, selected reviews of information on subjects of prevailing Commission interest as it becomes available.

This Review attempts to relate the published results of research and development sponsored by the Division of Isotopes Development to significant developments in radioisotopes and radiation technology, as reported in the world literature. Coverage includes isotope production and development, isotope technology development, isotope applications technology, process radiation development, and radiation processing of food and medical supplies.

In addition to reviews of current literature and special review articles dealing with specific isotopes, facilities, and applications, this publication occasionally contains feature articles prepared by recognized experts on specific topics of current interest. Critical evaluations and interpretations presented are those of the editors and invited reviewers; therefore readers are encouraged to consult the original references in order to obtain all the background of the work reported and the interpretation of the results given by the original authors.

Insofar as feasible all references are checked by the editors, using the library facilities of Oak Ridge National Laboratory, Oak Ridge Associated Universities, and the University of Tennessee. Occasionally, however, the cited material is not available; such cases are identified by an asterisk (*).

The subject headings listed below have been adopted to help maintain continuity and order, from one issue to the next, in the material reviewed. All reviews, except Feature Articles, will be arranged under these headings; but any one issue will not necessarily contain all the headings.

Isotope Production and Development
Isotope Technology Development
Food Irradiation
Process Radiation Development
Source Development
Isotopic Heat and Power Development
Applications in Life Sciences
Safety
Isotopes Around the World
Miscellaneous

P. S. Baker, Robert H. Lafferty, Jr., Martha Gerrard, R. E. Greene, F. E. McKinney, and Helen P. Raaen, *Editors*
A. F. Rupp, *Adviser*

OAK RIDGE NATIONAL LABORATORY

Issued quarterly by the U. S. Atomic Energy Commission. Use of funds for printing this publication approved by the Director of the Bureau of the Budget on December 16, 1968.

XUM

TECHNICAL PROGRESS REVIEWS

The United States Atomic Energy Commission publishes the Technical Progress Reviews to meet the needs of industry and government for concise summaries of current nuclear developments. Each journal digests and evaluates the latest findings in a specific area of nuclear technology and science. *Nuclear Safety* is a bimonthly journal; the other two are quarterly journals.

Isotopes and Radiation Technology
P. S. Baker, A. F. Rupp, and associates
Isotopes Information Center, Oak Ridge National Laboratory

Nuclear Safety
Wm. B. Cottrell, W. H. Jordan, J. P. Blakely, and associates
Nuclear Safety Information Center, Oak Ridge National Laboratory

Reactor Technology
Prepared in cooperation with the American Nuclear Society

All are available from the U. S. Government Printing Office. See the back cover for ordering instructions.

NOTICE

This journal was prepared under the sponsorship of the U. S. Atomic Energy Commission. Neither the United States nor the U. S. Atomic Energy Commission, or any of their employees, contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.

Availability of Reports Cited in This Review

United States Atomic Energy Commission (USAEC) reports are available at certain libraries that maintain collections of these reports. The libraries are listed on the inside front cover of each issue of *Nuclear Science Abstracts*. USAEC reports are also sold by the following governmental and international organizations: (1) National Technical Information Service (NTIS), U. S. Department of Commerce, Springfield, Va. 22151; (2) International Atomic Energy Agency (IAEA), Vienna, Austria; and (3) National Lending Library, Boston Spa, England.

Other U. S. Government agency reports identified in this journal are generally available from NTIS.

Reports from other countries are generally available at the same U. S. libraries as maintain collections of USAEC reports, and from IAEA and the originating country. **United Kingdom Atomic Energy Authority (UKAEA)** reports are sold by Her Majesty's Stationery Office, London. **Atomic Energy of Canada Limited (AECL)** reports are sold by the Scientific Document Distribution Office, Atomic Energy of Canada Limited, Chalk River, Ontario, Canada. UKAEA and AECL reports issued after March 1, 1967, are sold by NTIS to purchasers in the United States and its territories. IAEA publications are sold in the United States by UNIPUB, P. O. Box 433, New York, N. Y. 10016.

Private-organization reports should be requested from the originator.

The views expressed in this publication do not necessarily represent those of the United States Atomic Energy Commission, its divisions or offices, or of any Commission advisory committee or contractor.

XU

Section I

Isotopes and Radiation Technology

Isotope Production and Development

Fission-Product Xenon and Krypton—An Opportunity for Large-Scale Utilization*

By C. A. Rohrmann†

Supplementary Keywords: *fission product, stable; reactor by-product recovery; industry; nuclear energy; industry, electric; medicine; economics; isotope abundance; production, radioisotope; ionization of gas; pollution; atmosphere; review, technical; comparison; safety; hydrogen-3; krypton-85.*

Abstract: *In the near future, xenon, as a fission product from nuclear-fuel processing, could be made potentially available in great quantities and at low costs compared to those of xenon from today's conventional liquid-air-processing sources. One year after discharge from a reactor, the fission-product xenon contains only insignificant amounts of activity from short-lived xenon radioisotopes. Residual activity will depend almost totally on the effectiveness of the krypton separation in removing the highly radioactive ^{85}Kr. Present technology appears capable of ensuring such removal. Comparisons of future fission-product and atmospheric xenon resources and costs are made. Physical properties of xenon and krypton are discussed. If the price becomes competitive, xenon may replace krypton in some applications, for example, as an inert gas in incandescent lamps. Another attractive major potential use of xenon is as an agent in surgery, where it has been found to be applicable in human anesthesia.*

Until recently interest in and activity on materials recoverable as by-products of atomic energy operations or producible via nuclear reactions have been almost exclusively confined to the radioisotopes. The use of these exciting materials in medical research and technology, in life-science studies generally, and in industrial technology has indeed brought great benefits. In addition, the space-power potentialities of massive quantities of the longer lived radioisotopes that can be made available are also spectacular. The use of intense radiation sources in food processing for preservation and disinfestation is an exciting application that has also received concentrated research and development study.

However, more than 20 years after most of these applications were first explored, none of them holds much promise for consuming the large quantities of even the most attractive radioisotopes which are today already in great supply and which in the future will continue to accumulate at a rapidly accelerating rate in the residues from nuclear-fuel processing.[1] As a result of this developing situation, which has been emphasized by the long-range Battelle–Northwest studies of the development of the nuclear power industry, more consideration has been given by Battelle–Northwest[2] since about 1962 to the practical applications of the few, essentially stable, now rare and very costly, useful elements that are produced in fairly high yield from the fission process. Today probably no more than three of these elements can be considered—rhodium, palladium, and xenon.

These three elements are readily available articles of commerce; and, as such, they have many important common uses in man's everyday living: attractive platings on inexpensive jewelry, dental alloys, household-appliance control equipment, telephone switchgear, photo flashtubes, and ultraviolet and other intense light sources. In addition, there are extremely important large-scale industrial uses for each of these. Xenon is used in multikilowatt intense-light sources[3] and special high-power electronic equipment. Both rhodium and palladium have very essential and wide-

*This article is based on work performed for the Division of Isotopes Development, U. S. Atomic Energy Commission.

†Division staff engineer, Chemistry and Metallurgy Division, Pacific Northwest Laboratory (Battelle–Northwest), Battelle Memorial Institute, Richland, Wash.

XUM

spread applications for catalysts and alloys and in communications switchgear.

There would very likely be an extension of the applications for these very useful materials if greater availability and lower costs could be ensured. This conclusion is probably more appropriate for xenon than for the others. Fission-product rhodium and palladium were reviewed in the Summer 1969 issue of this journal.[4] The present article discusses fission-product xenon and krypton. It should be emphasized that the applicability of these fission-derived, essentially stable, and valuable elements is not a new disclosure; references can be cited on the subject dating back many years.[5] Unfortunately some of the most significant references are still classified and hence are not identified here. However, the recent rather sudden and massive advances in civilian nuclear-power development in the United States and the accompanying plans for early construction of fuel-processing plants of capacities far greater than were proposed even as late as 2 years ago make review of the quantities and applications of these by-products timely, appropriate, and unique.

For many years argon has been used to fill (at about atmospheric pressure at operating temperature) all tungsten-filament light bulbs because it depresses the vaporization of the tungsten filament and thus promotes the attainment of higher filament temperature, brighter light, and prolonged filament life. According to Fastovskii, Rovinskii, and Petrovskii,[6] this use alone consumed 400 million liters of argon in the United States in 1958. Also for many years krypton has been looked upon as a desirable replacement for argon in special long-lived light bulbs. The higher atomic weight of krypton makes it even more effective than argon in depressing the vaporization of tungsten. Its lower thermal conductivity also contributes to smaller bulb size, brighter light, and longer life for the filament. In Europe, krypton has been used in this way for many years. Recently there has been a shift toward the use of oxygen instead of air for the operation of basic open-hearth steel furnaces in the United States; liquid-air plants, some supplying as much as 1000 tons of O_2 per day, provide the required oxygen. Only with this shift has sufficient liquid-air capacity become available to ensure, at fairly reasonable cost, the volumes of krypton required by a reasonably large-scale lamp-production operation.

In early summer 1968, two companies announced their intention of marketing long-lived 60- and 100-W krypton-filled bulbs.[7] Such bulbs were available later in the year. The price range of about $0.70 to $1.30 reflects the specialty nature of these bulbs rather than the actual cost of the gas used. This application alone could probably consume all the krypton that could be recovered from the very-large-scale oxygen industry. The small quantity of xenon recoverable along with krypton from these liquid-air-processing operations would still be insufficient (and thus probably too costly) to provide the practical amounts for such large-scale applications. However, xenon would be significantly superior to krypton in this application because of its much higher atomic weight and lower thermal conductivity (Table 2). It is certain from a review of xenon applications that the extreme rarity and high cost of this element have inhibited consideration of it even in some applications where it may be superior.

Xenon is produced in reactor fuels in the highest yield, on a weight basis, of all the elements produced by the fission of uranium and plutonium. The application of this fission-derived xenon, which will be available in less than 10 years in fairly large amounts (Fig. 1) from the large nuclear-fuel-processing plants, is a distinct and encouraging possibility that has initiated interest in this review article. However, even if all available atmospheric krypton and xenon and fission-product xenon were used by the incandescent-lamp industry, the use of argon[6] would not be appreciably diminished now or in the future. Under any conceivable development, krypton and xenon will always be rather rare and fairly costly materials.

Although the useful properties of xenon have been well known for many years, the most surprising

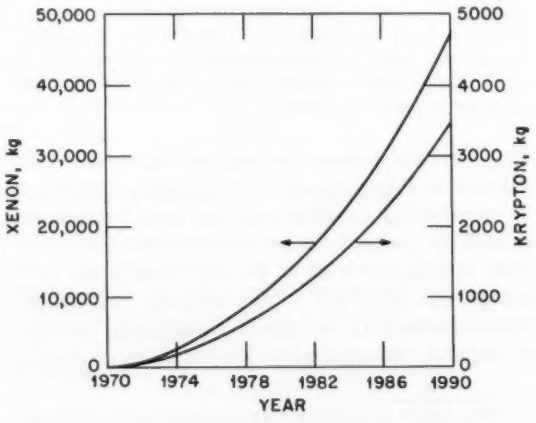


Fig. 1 Projected annual recovery of fission-product xenon and krypton from U. S. power-reactor-fuel processing plants (based on data in Ref. 1).

application for which xenon appears to be unique among the inert gases and specific to man is in producing anesthesia. This property has been known for about 20 years. But here again xenon's rarity and very high price preclude its use for this large-scale beneficial application except in experimental or theoretical studies. Cullen and Gross[8] in 1951 are credited with the first use of xenon as an anesthetic for surgical procedures on man. Their gas mixture comprised 18 to 22% oxygen, the balance being high-purity xenon. This anesthetic gas was essentially a synthetic air in which all the nitrogen had been replaced by xenon. In a review on inert-gas anesthesia, Featherstone and Muehlbaecher[9] reported the following observations on the use of xenon as an anesthetic for man: In one case of light anesthesia, there was no evidence of reaction to pain and full recovery was noted in 5 min. In another case a satisfactory degree of anesthesia was achieved within a few moments. Excitement during administration was absent, and recovery occurred in 2 or 3 min after the administration of xenon was stopped. Man was the only species that could be anesthetized with the xenon gas mixture at atmospheric pressure. Other animals (monkeys and dogs) can be anesthetized with xenon mixtures but only at elevated pressure (2 to 3 atm). Xenon-induced anesthesia is characterized by the unusual brevity of the induction and emergence periods. Equivalent mixtures using krypton were ineffective when administered to human subjects.

DISCUSSION

Xenon Resources and Properties

Atmospheric. Xenon is one of the six so-called "inert" gases* (which include He, Ne, Ar, Kr, and Rn) that occur in the atmosphere. Only radon is naturally radioactive, but it has such a short half-life (3.8 days for its longest lived isotope) that it can be neglected as a constituent recoverable from the atmosphere. Of the others, only helium occurs in practical concentration in nonatmospheric sources. By far the most important source of helium is certain fuel-type natural gases, from which it is routinely extracted commercially in large quantities. Fastovskii, Rovinskii, and Petrovskii[6] tabulated the abundance of these rare gases in air (Table 1). Other properties of these gases are given in Table 2.

*Also called rare or noble gases.

Table 1 Composition of Dry Air

Gas	Amount in air		Relative abundance (Xe = 1)	
	Vol.%	Wt.%	By volume	By weight
CO_2*	0.033	0.050	3,840	1,282
Helium	5.239×10^{-4}	0.724×10^{-4}	61.00	1.86
Neon	1.818×10^{-3}	1.267×10^{-3}	211.5	32.5
Argon	0.934	1.288	108,700	33,000
Krypton	1.14×10^{-4}	3.29×10^{-4}	13.25	8.44
Xenon	0.86×10^{-5}	0.39×10^{-4}	1.0	1.0

*Although CO_2 is not a rare gas, it is included for comparison since it is a minor constituent in the atmosphere where it is far less prevalent than is argon.

Table 2 Some Properties of Inert Gases

Gas	Atomic weight*	Density (STP), g/liter	Boiling point of liquid, °K	Heat of vaporization at b.p., cal/gram mole	Heat capacity (1 atm, 20°C), cal/(g)(°C)	Thermal conductivity (1 atm, 50°C), cal/(cm)(°C)(sec)
Neon	20.179	0.9003	27.07	414	0.248	15 (est.)
Argon	39.948	1.7839	87.27	1558	0.125	4.62
Krypton	83.80	3.745	119.80	2258	0.0594	2.41
Xenon	131.30	5.897	165.05	3020	0.0378	1.47

*From Ref. 10.

On the basis of the data in Table 3 the average atomic weight of fission-product xenon will be about 134.3 or more (vs. 131.3 for natural xenon). Likewise, the average atomic weight for fission-product krypton will be about 85 (vs. 83.8 for natural krypton).

Fission Product. Fission events from either ^{235}U or ^{239}Pu produce approximately 40 elements including many isotopes of some elements (about 18 for xenon). The radioactivities of these various isotopes range from none to highly radioactive. Some of the

Table 3 Isotopic Composition

Xenon			Krypton		
Isotope	Natural,* at.%	Fission product,† at.% (approx.)	Isotope	Natural,* at.%	Fission product,† at.% (approx.)
124	0.096	–	78	0.354	–
126	0.090	–	80	2.27	–
128	1.92		82	11.56	0.2
129	26.44	0.15	83	11.55	11
130	4.08		84	56.90	31
131	21.18	8	85	–	6
132	26.89	22	86	17.37	52
134	10.44	29			
136	8.87	41			

*From Ref. 10.
†From Ref. 11.

The data on the concentration of xenon and krypton in air indicate the rarity of these gases. Obviously, recovery of even reasonable amounts at low cost requires the processing of enormous tonnages of air. The switch from air to oxygen in the steel industry is continuing with the building of large liquid-air plants.[12] Although these plants generally do not yield separated xenon and krypton, the opportunity now exists to provide, at rather modest cost, additional facilities by which the xenon and krypton could be recovered in fairly high yields (85%) from intermediate concentrates that can be readily separated. Large-volume sales[13] of krypton are now being made at about $0.50 per liter. As demand and production increase, lower prices are anticipated. A similar though less impressive situation should also come about from xenon. One-thousand-liter orders for xenon (STP) can be filled today for about $10 per liter and smaller quantities for $20 to $35 per liter.[14] The small scale of present consumption is understood to be rather insensitive to price. With increased krypton production and consumption, the accompanying xenon [about one-thirteenth as much on a volume basis (Table 1)] will seek its own market-price level, probably appreciably below the $10 figure; however, it is highly unlikely ever to be less than the price of krypton from this source.

radioactive species have half-lives so long and emission energies so weak that they can be regarded as essentially stable materials—e.g., ^{129}I has a half-life of 1.6×10^7 years, and ^{147}Sm, ^{148}Sm, and ^{149}Sm have half-lives in the range of 10^{11} to 10^{14} years (the last isotope having only one-millionth of the activity of ^{235}U). On the other hand, there are many radioisotopes of intense activity, but their half-lives are so short that they can be disregarded since their concentrations would be insignificant under practical conditions of large-scale recovery. For low-enrichment uranium or plutonium fuels exposed to about 25,000 MWd/metric ton, fission-yield calculations indicate production of nearly 4 kg of xenon per metric ton. All radioactive fission-product xenon isotopes have half-lives so short (12 days maximum) that no normally detectable xenon radioactivity will exist beyond 1 year after the fuel is discharged from the reactor. Thus fission-product xenon can be regarded as being entirely stable xenon isotopes. Any radioactivity present will depend on the effectiveness of the process by which xenon is separated from contaminating material, specifically, fission-product krypton (containing about 6 at.% ^{85}Kr, half-life 10.76 years). The fission-product krypton, including the intensely radioactive ^{85}Kr, will exist in the same fuel at about 0.25 kg/metric ton. Although other gases are produced

XUM

in fission, their concentrations will be extremely small. Depending on the dissolution process used and the effectiveness of minimizing extraneous gas (air) inleakage, the vent gases could conceivably be a nearly pure mixture—extremely rich (compared to liquid-air-process conditions) compositions of xenon and krypton.

At this point another comparison is worth reviewing: xenon and krypton production from an oxygen plant and from a nuclear-fuel-processing plant. As shown in Table 4 the typical fuel-processing plant, to be in operation in about 5 years, has a xenon capability on a volume basis about $12\frac{1}{2}$ times as great as that from today's largest oxygen plant. Another view is that on a volume basis the production capability for xenon from a typical fuel-processing plant is essentially the same as the krypton production capability from today's largest oxygen plant.

Another impressive comparison may be made: A 5000 ton/day air-separation plant (1000 tons of oxygen per day) will, at 300 operating days per year, require 4 years to process 1 cubic mile of air to recover 360 m^3 of xenon. A 5 ton/day fuel-processing plant will yield the same amount of xenon in less than 6 months (113 operating days).

It is concluded from these examples that fission-product xenon will become available via reactor-fuel-processing operations in quantities sufficient to ensure consideration as a marketable product. Not only will fuel processing provide large quantities at an ever-increasing annual rate as nuclear power production assumes a larger fraction of the world's power needs, but also this xenon could be available from the primary source in relatively very high concentrations—conceivably several percent in the primary waste gas.

Another facet of this fission-product xenon resource relates to the problem of air pollution. This problem is not, of course, concerned with any pollution aspects of xenon itself but specifically those from the companion rare gas, radioactive ^{85}Kr. (It is emphasized that the author professes complete neutrality with regard to whether or not the release of fission-product krypton with its 6% fraction of ^{85}Kr represents a significant air pollutant and therefore whether or not fuel-processing plants should be required to trap and contain it.) In view of its inertness, ^{85}Kr should have no exposure relationship to any specific organ. Its hazard, which incidentally on a maximum-permissible-concentration basis is listed among the least hazardous of all radioisotopes, would relate entirely to environmental exposure for a body completely surrounded or immersed in an atmosphere containing the ^{85}Kr. With the assumption of complete, rapid, and uniform mixing in the earth's total atmosphere, calculations can show that the hazard of fission-product krypton does not appear to be significant for the foreseeable future. Nevertheless, on a curie basis ^{85}Kr will contribute far more activity than any other isotope routinely released to the environment from the fuel-processing plant. A 5 metric ton/day fuel-processing plant consuming feed irradiated to 25,000 MWd/metric ton could be releasing ^{85}Kr activity amounting to about 35,000 Ci/day. In the license applications made by both the General Electric Company and the Allied Chemical Corporation for their proposed fuel-processing plants, no facilities were identified which would be used to trap the krypton. Similarly, at this time no such processes are known to be in operation or planned for any of the other private fuel-processing plants (Nuclear Fuel Services, Inc., National Lead Company, or Atlantic Richfield Company). In other words, at this time there are no provisions for fission-product radiokrypton disposal from nuclear-fuel-processing plants other than by venting to the atmosphere.

Table 4 Comparison of Xenon and Krypton Production in Oxygen and Fuel-Processing Plants

Plant	Krypton, liters (STP)	Xenon, liters (STP)	Krypton in mixed gas, vol.%	Xenon in mixed gas, vol.%
Oxygen (10^3 short tons/day, 85% recovery)	3400	255	93	7
Fuel processing (5 metric tons/day,* 95% recovery)	326	3210	9	91

*Irradiated to 25,000 MWd/metric ton.

If, however, for pollution-abatement reasons there were to develop a requirement for ^{85}Kr trapping, the impact on fission-product xenon availability and economics could be extreme and highly favorable. (Again the statement here should not be construed as favoring such action. It is merely made to illustrate what the influence could be on the future of fission-product xenon.) If ^{85}Kr had to be trapped and perpetually stored, the small volumes of krypton compared with the volumes of xenon would for economic reasons ensure that these two gases would be separated to save on ^{85}Kr storage costs. (The mixed inert fission gas would be only about 9% krypton.) If these conditions were to prevail, xenon costs could relate only to the expense involved in diverting it as highly concentrated gas and in refining it to remove the residual ^{85}Kr to tolerable levels. Present rare-gas-processing techniques can ensure separations down to the few-parts-per-million level—normally 20 ppM, with 5 ppM achievable; however, techniques are available which could ensure far lower levels. For fission-product xenon that has been out of the reactor for 1 year, any activity associated with remaining short-lived xenon isotopes is expected to be less than 10^{-10} Ci per liter of gas (STP). Such activity is not regarded as significant for any large-scale consumer applications. Furthermore, this activity would diminish by one-half every 12 days. The residual radiation is thus dependent on the effectiveness of ^{85}Kr removal. Based on the assumption that fission-product krypton contains 6% ^{85}Kr and a xenon product contains 5 ppM of total krypton contamination, the activity of the xenon on a volume basis will be about 450 μCi per liter, or 45 μCi per 100 ml, which may be the maximum volume of the consumer product in the incandescent lamp bulb. This quantity of activity in this product does not appear to be sufficient for its rejection, but further study with respect to a permissible dose rate and the feasibility of further purification should be considered. At the present time, means appear to be at hand to reduce ^{85}Kr contamination to possibly 1% of the levels indicated above or to 1 to 10 μCi/liter. Recent work on a Division of Isotopes Development program at Oak Ridge National Laboratory to purify several hundred liters of fission-product xenon has yielded material containing only 2 μCi of ^{85}Kr per liter of xenon.

Uses of Xenon and Krypton

A Linde Air Products Company brochure[15] on the uses of xenon and krypton indicates that krypton is used to fill tiny incandescent lamps where high efficiency is demanded. The heavier weight of krypton gas decreases filament vaporization and heat losses, permitting higher temperature operation of the lamps. The introduction of krypton gas as a filling agent in fluorescent lamps has increased their efficiency by 10%. Krypton is also used in high-intensity airport landing-approach lights.

According to the brochure, xenon is used in thyratron tubes, where its temperature insensitivity is essential. The excellent spectral characteristics of the xenon arc are utilized in high-speed photographic lamps. The anesthetic properties of xenon are also mentioned. Its inertness may provide safety features unobtainable with some other types of anesthetic gases.

None of the uses described here would lead to large-scale applications, and thus no consideration appears to be advanced for utilization of the massive quantities of relatively low-cost rare gases obtainable from either the enormous oxygen production plants or from the modest-sized fuel-processing plants which are certain to be operating in the near future. The specialty incandescent-lamp industry could probably consume all the krypton obtained from the large-scale oxygen industry. The xenon, obtained concurrently with krypton, probably could not be considered for this application because of the small quantity recovered and its price.

The xenon recoverable from nuclear-fuel-processing plants could, however, very likely be considered competitive with krypton for this same application. The cost of xenon should be comparable with that of krypton, and xenon availablilty should be significant. However, the use of xenon as an anesthetic gas may be an even more logical use. Such a beneficial application may also support a substantially higher price, especially if the gas can be used in closed or recycle-type systems, which, we understand, require only about 8 liters of gas for a single operation. The selling prices of such gases should, of course, determine the application and the magnitude of the use. Thus, for fission-product xenon, there are conceivable conditions under which a very-low-cost product could be ensured. From this source the selling price goal should be in the range of \$0.50 to \$1.00 per liter (STP) of purified gas to be competitive with krypton; however, for anesthetic uses the price may be in the range of \$1.50 to \$3.50 per liter.

Although comments above on fission-product krypton have related exclusively to its removal and permanent confinement to avoid discharge of activity

XUM

to the environment, ^{85}Kr must be regarded as a unique material. Special applications for it have been considered and are still appropriate. The proposed applications relate to the use of its beta activity in lighting in assisting the starting of fluorescent lamps and as the activator in special phosphorescent lamps. Krypton-85 has also been suggested as a heat source, but in this application isotopic enrichment from the existing 6% to about 50% for ^{85}Kr is almost essential. A low-cost enrichment process does not appear to be achievable at present. Therefore the prospects for such an application do not appear very hopeful. However, consideration of the use of the intense beta activity of this unique gas should be receiving more intensive study, particularly in view of its future potentially low cost.

COST, VALUE, AND PRICE

The following discussion on cost, value, and price is relevant to the possible exploitation of fission-product xenon and krypton. At today's prices there are few private needs that can consume much xenon. The few special uses of this gas, such as in high-intensity lamps and electronic tubes, could probably tolerate an even higher price. However, such uses cannot possibly consume all the xenon that could be obtained just from the many large liquid-air plants now in operation. It is also conceivable that fission-product xenon could be recovered very profitably at $10 per liter today. However, as noted above, few markets exist for xenon of such value or price. In 1980, at the $10-per-liter price, about $20 million worth of fission-product xenon will be released from spent fuel processed for the nuclear power industry. It is inconceivable that the small specialty uses for xenon could expand to the level which would require either that quantity or that investment in xenon. A much more realistic view of the market possibilities must be taken. For example, at present, only two uses can be foreseen which could consume all fission-product xenon—as an inert atmosphere in long-lived tungsten-filament incandescent lamps and as an anesthetic. For incandescent lamps xenon would have to compete with krypton. In this use xenon would be somewhat superior and could command a higher price, but not much higher—probably much less than double the price of krypton since it is better but can be expected to be only fractionally better.

With continued expansion in large-scale oxygen recovery and competition in the marketing field, a lower price can be expected for krypton in the future with stabilization perhaps in the $0.25 to $0.50 per liter range by 1980. For xenon to be competitive in this large-scale application, a price somewhat above this range can be expected to be acceptable. All xenon should then be marketable at a price range starting at $0.50, but definitely less than $1 per liter. At this price range the total fuel-processing industry might anticipate the revenue from xenon to lie between $0.5 and $2 million in 1980. If venting of krypton to the atmosphere must be restricted, xenon pricing in the above range may be definitely attractive and significant but not a major source of revenue. In the use of xenon as an anesthetic, the unique and advantageous properties of this gas may minimize the competition from conventional anesthetics. For this use then xenon may justify a higher price, probably $1.50 to $3.00 per liter.

If one can conceive of a market for fission-product krypton, an even more drastic scaledown of price or value must be accepted. For example, if it is assumed that fission-product krypton with its 6% ^{85}Kr could be used in improved fluorescent lighting for general and uncontrolled use in homes and that only a small fraction of a curie of activity from ^{85}Kr is contained in each device, then possibly such an application could consume all that could be obtained.

The present price[16] for fission-product krypton is $22 per curie. At this price the value of the total amount available from nuclear-fuel-processing plants in the United States in 1980 would be about $500 million! It is, of course, inconceivable that uses will be developed by 1980 which could justify such investments in this radioisotope. Tritium (^{3}H) can be had for $0.75 per curie today on orders greater than 25,000 curies.[16] Tritium may be a more versatile radioisotope with potentially more uses than ^{85}Kr. The latter isotope should then be priced lower—probably much lower. Such prices could be of interest in fuel processing only if trapping and indefinite retention of ^{85}Kr were already a requirement for antipollution reasons. At a price as low as $0.08 per curie, the revenue from ^{85}Kr in 1980 would be about the same as that for xenon at the upper level of its lower price projection. The concept of distributing the total production of ^{85}Kr in the form of fluorescent lamps, each containing a few millicuries of activity, may be a more acceptable solution to the disposal problem than first thoughts may indicate. Although radioactivity is present, it is never directly in contact with any part of the human body. Furthermore, with modern ventilation in homes, offices, and industrial facilities, the occasional rupture of a bulb containing a few millicuries of ^{85}Kr does not appear to present a

critical hazard. A statistical view of this situation may indicate that this is an acceptable method of ^{85}Kr disposal.

However, for utilization of either fission-product xenon or krypton, the low projected prices must assume that facilities are required for krypton trapping and retention as a pollution-control effort. Under such conditions the revenues that may be realized are attractive but definitely modest. (REG)

REFERENCES

References marked with an asterisk have not been verified by the editors; for further explanation, see the Foreword.

1. D. E. Deonigi, R. W. McKee, and D. R. Haffner, Isotope Production and Availability from Power Reactors, USAEC Report BNWL-716, Pacific Northwest Laboratory, July 1968.
2. M. M. Hendrickson and J. K. Green (Eds.), Research and Development Programs Executed for the Division of Reactor Development, Quarterly Progress Report, October–December 1962, USAEC Report HW-76559, Hanford Atomic Products Operation, January 1963.
3. G. S. Hunter, Airborne Illumination Development Spurred by Viet Needs, *Aviat. Week Space Technol.*, 89(17): 92-94, 99, 102-103 (Oct. 21, 1968).
4. C. A. Rohrmann, Large-Scale Exploitation of Fission-Product Rhodium and Palladium, *Isotop. Radiat. Technol.*, 6(4): 352-358 (Summer 1969).
5. E. Glueckauf, The Long-Term Aspect of Fission Product Disposal, *Atomics and Atomic Technol.*, 6(9): 270-276, 281 (1955). See p. 275, Table III.
6. V. G. Fastovskii, A. E. Rovinskii, and Yu. V. Petrovskii, *Inert Gases*, USAEC Report AEC-tr-6725, translated from the Russian by J. Schmorak, Jerusalem, Israel Program for Scientific Translations, 1967.
7. Krypton May Battle Argon for the Incandescent Lamp Market, *Chem. Week*, 102(25): 78 (June 22, 1968).
8. S. C. Cullen and E. G. Gross, The Anesthetic Properties of Xenon in Animals and Human Beings, with Additional Observations on Krypton, *Science*, 113: 580-582 (May 18, 1951).
9. R. M. Featherstone and C. A. Muehlbaecher, The Current Role of Inert Gases in the Search for Anesthesia Mechanisms, *Pharmacol. Rev.*, 15: 97-121 (1963).
10. Chart of the Nuclides, Tenth Edition—Revised to December 1968, Knolls Atomic Power Laboratory, General Electric Company, 1968. (See also Battelle–Northwest modified version of this reference, May 1970.)
11. W. A. Bezella, Analysis of the Fission Gases Released Within Spent Yankee Fuel Rods, USAEC Report WCAP-6087, Westinghouse Electric Corp., February 1968.
12. New Plants and Facilities, *Chem. Eng.*, 74: 188-190 (Apr. 10, 1967) and 223-224 (Oct. 9, 1967).
13. Materials Applications, *Ind. Res.*, September 1968: 49-50.
14. *AIRCO Rare and Specialty Gases, catalog of Air Reduction Co., Inc., 150 E. 42nd St., New York, N. Y. 10017, 1968, p. 18.
15. Linde Rare Gases, Brochure, Linde Air Products Company, Union Carbide Corporation, 270 Park Avenue, New York, N. Y. 10017.
16. Private communication, November 1970, Isotopes Sales, Building 3037, Isotopes Development Center, Oak Ridge National Laboratory, P.O. Box X, Oak Ridge, Tenn. 37830.

^{90}Sr Heat Sources

By Roberta Shor, R. H. Lafferty, Jr., and P. S. Baker

Supplementary Keywords: *production, radioisotope; production, separation; reactor by-product recovery; source preparation; source, beta; source, bremsstrahlung; industry, radioisotope; energy source; conversion, electric; thermoelectric system; tracer; leak detection; safety, container; chemical property; physical property; original research; review, technical; data compilation; pilot plant scale; unusual condition; strontium-90; krypton-85.*

Abstract: *Current methods for the purification of fission product ^{90}Sr and the production of ^{90}Sr fuel forms are described. The SNAP-7A fuel is examined after 5½ years of operation. Excerpts were made from a full-length report on ^{90}Sr heat-source production, source testing, and source properties.*

Compact electric generators powered by heat from radioisotopes have been under development in the United States since the early 1950s for space, marine, and terrestrial uses. Essentially all the generators developed for marine and terrestrial uses[1,2] have been powered by ^{90}Sr. The preparation of ^{90}Sr fuel forms, beginning with spent reactor fuel wastes and ending with the encapsulated fuel, is described in a comprehensive report now in preparation, which will be available on request from the Isotopes Information Center, Oak Ridge National Laboratory. The highlights of the report are presented here. The report summarizes the developmental work done by Oak Ridge

XUM

National Laboratory (ORNL), Hanford Atomic Products Operation (Hanford*), and Martin Company, Nuclear Division, which led to the production of ^{90}Sr heat sources for use in the generators.

The processes discussed include:

1. Separation of radiochemically pure ^{90}Sr from the reactor wastes in a chemical form suitable for further processing.
2. Conversion of the separated ^{90}Sr to a chemical form suitable for a heat source.
3. Fabrication of the separated chemical compound into pellets having a suitable density and purity for a heat source.
4. Encapsulation of the pellets in a metal container that is resistant to corrosion by the source compound and by the environment in which it is to be used.

Generator design is excluded, except as it relates to the properties of the fuel forms required in the generators.

SELECTION OF ^{90}Sr AS HEAT SOURCE

Several qualities make ^{90}Sr attractive as a fuel for heat sources:

1. It is available in large amounts in the wastes resulting from the processing of spent reactor fuels.
2. Procedures for recovering ^{90}Sr of high radiochemical purity with low inert-contaminant levels have been developed.
3. Its half-life is 28.5 years.
4. Fuel forms can be made from fission-product wastes with adequate power density for applications in power-generator heat sources. Pure ^{90}Sr has a specific activity of 139 Ci/g and a specific power of 0.0067 W/Ci; however, fission-product (FP) strontium contains only 55 at.% ^{90}Sr. Achievable power densities are limited by the age of the FP ^{90}Sr, the amounts of inert contaminants present, and the deviations of the fuel materials from theoretical physical density.

Several chemical forms of ^{90}Sr fuel were considered—$SrTiO_3$, SrF_2, SrO, Sr, and Sr_2TiO_4. The properties that outweighed all others in the selection process were the power density, thermal stability, and solubility—particularly in seawater. The compound offering the most desirable combination of properties was $SrTiO_3$, and it has been used in fabricating most of the ^{90}Sr heat sources to date.[3,4] Of the compounds considered, $SrTiO_3$ is the least soluble in water, and its power density (0.7 to 0.9 W/cm^3, depending on the method of preparation) is sufficient to meet generator design needs for present applications. The only other compound that has been used as a heat source is SrO, although SrF_2 is being considered as a storage form. The power density of SrO is ~1.6 W/cm^3, but it is moderately soluble in water. Both compounds can be prepared by simple procedures adaptable to manipulator-cell operations. Handling and storage problems are simpler for $SrTiO_3$ than for SrO, but decontamination of cells where $SrTiO_3$ is handled is more difficult.

Modern thermoelectric generators use semiconductor materials made into *n*- and *p*-type legs. The legs are cylinders bonded to hot and cold "shoes." The heat from the isotope source (^{90}Sr) flows into the hot shoe and moves up through each element to the cold shoe and into the cold reservoir. The difference in potential across the *p* and *n* elements is proportional to the difference in temperature between the hot and cold reservoirs. The maximum hot temperature and the efficiency of the generators depend on the material used for the thermoelements. The generators now in operation use lead telluride elements in an inert-gas atmosphere and operate at temperatures up to ~530°C. The *p* and *n* elements are made from lead telluride having small differences in composition.[1] A 5% efficiency in converting heat to electric energy is the highest achieved in the generators built in the SNAP-7 (Systems for Nuclear Auxiliary Power) program. The expected maximum efficiency for terrestrial application is 10% if GeSi and PbTe thermoelements in a cascade arrangement operate at 750°C with 130°C cold junctions.[5]

In August 1961 the first ^{90}Sr-powered automatic weather station was placed on Axel–Heiberg Island in Canada, 700 miles from the North Pole. The unmanned station, designed to collect and relay data on temperature, wind velocity, and barometric pressure, was part of a joint project of the U. S. and Canadian weather bureaus. It operated successfully until August 1964 (Ref. 2).

The six generators in the SNAP-7 series (Table 1) were designed after demonstration of the Axel–Heiberg weather bureau station and were similar to it and to each other in most respects. The sources for these generators were fabricated[1] by ORNL and Martin

*Hanford Atomic Products Operation of General Electric Company was divided in 1965 and 1966 among a number of contractors. For simplicity and convenience in this report, all the work done at Hanford is referred to as Hanford work. No effort has been made to identify the particular contractor responsible for the later work. However, the reports cited in the references are so identified.

Table 1 Status of ^{90}Sr-Powered Thermoelectric Generators* (1970)[1,2,4,6-8]

Name	Kilocuries	Power, W		Date installed	Buyer	Use	Place	Contractors	Comments
		Thermal	Electric						
Sentry (Weather Bureau)	17.5	110	5	1961	Weather Bureau	Weather station	Axel-Heiberg Island	Hanford, ORNL, Martin	Operated 3 years; no ^{90}Sr failure
SNAP-7A	41	250	10	1962	U. S. Coast Guard	Buoy light	Curtis Bay, Md.	Hanford, ORNL, Martin	Gradual power loss greater than design predicted; disassembled April 1969
SNAP-7B	220	1400	60	1964	U. S. Coast Guard	Lighthouse	Baltimore, Md.	Hanford, Martin	Replaced SNAP-7F in 1965
SNAP-7C	41	250	10	1962	U. S. Navy	Weather station	Antarctic mainland	Hanford, ORNL, Martin	Dismantled November 1967
SNAP-7D	225	1400	60	1964	U. S. Navy	Barge weather station	Gulf of Mexico	Hanford, ORNL, Martin	Auxiliary equipment failure
SNAP-7E	30	180	7.5	1964	U. S. Navy	Sonic beacon	Undersea near Fla.	Hanford, ORNL, Martin	Failure of pinger in 1968
SNAP-7F	225	1400	60	1965	Phillips Petroleum and AEC	Buoy warning and control station	Gulf of Mexico	Hanford, Martin	Shield failed; seawater ruined thermoelements
URIPS (P1-1002) (P1-1001A)	7	45	1	1966 1967	U. S. Navy	Deep sea	Port Hueneme, Calif.	Hanford, ORNL, AGN	In storage, 1969
NUMEC (2)	30	200	7	1966	Israel	Undersea or surface		Hanford, ORNL, NUMEC	
U1-1001	7	45	1	1967	Joint venture: AGN-BMI-Bendix	Geodetic bench mark	Pacific Ocean near Anacupa Island	Hanford, ORNL, AGN	First license for deep-ocean non-recovery use
NUMEC 100 MA (2) milli TRACS	2.7		0.1	1967	U. S. Navy	Deep sea	Port Hueneme, Calif.	Hanford, ORNL, NUMEC	
NUMEC TRACS-25A	118		20	1968	U. S. Navy	Tidal-wave warning system	Bahamas	Hanford, ORNL, NUMEC	

RIPPLE III	4.6		0.7	1967	U. S. Navy (loan)	Undersea test	Port Hueneme, Calif.	Hanford, ORNL, UKAERE	
RIPPLE IV	15	100	2			Submarine cable repeater		Hanford, ORNL, UKAEA, and Submarine Cables Ltd.	
RIPPLE IX	30	200	4			Aircraft ground radio beacon	Outer Hebrides Islands	Hanford, ORNL, UKAEA, and Submarine Cables Ltd.	
MW-3000A	20		2.5	1967	U. S. Navy	Deep sea		Hanford, ORNL, Martin	
SNAP-21 (5 made)	40	200	10	1969	U. S. Navy	Undersea	Offshore San Clemente Is., Calif.	Hanford, ORNL, 3M	
LCG 25A	110	740	25	1966	U. S. Navy	Oceanographic instruments	Fairway Rock, Alaska	Hanford, ORNL, Martin	
LCG 25B			25	1967	U. S. Navy		Port Hueneme, Calif.		
SNAP-23A	200	1200	60	1969	U. S. Navy	Terrestrial		Hanford, ORNL, Westinghouse	
Sentinel 25E (11, 12, 13)	106 each	700	25	Mar. 1969	U. S. Navy	Oceanographic data stations		Hanford, ORNL, Isotopes, Inc.	
Sentinel 25D (8, 9, 10)	106 each		25	June 1969	U. S. Navy	Terrestrial and to 1000-ft undersea buoys		Hanford, ORNL, Isotopes, Inc.	
LCG 25C1	110	740	25	1968	NASA	Interrogation, recording, and location system	Puerto Rico coast sub-surface buoy	Hanford, ORNL, Martin	Failure in auxiliary equipment; reinstalled off Calif. coast at San Diego
P1-1003 P1-1004 P1-1005 P1-1006	8	53	1.2	1970	USN	Deep ocean	Port Hueneme, Calif.	Hanford, ORNL, AGN	Qualified for 35-thousand-ft ocean depth

*A FORTRAN computer program for use by Naval Facilities Engineering Command personnel makes available information concerning the various radioisotope power devices. The 31 data items applying to any device are described in U. S. Naval Power Unit, Quarterly Operating Report for Radioisotopic Power Devices of the U. S. Navy, Vol. 4, No. 3, pp. 7-8, 1970.

from ~1 MCi of ^{90}Sr that had been separated at Hanford in 1961.

The promising experience with the SNAP-7 series led to an expansion in AEC's plans for ^{90}Sr devices ranging in power from 0.1 to 10 kW(e). The technology developed in the earlier programs made it possible to design a more flexible generator system. The isotopic power program is now organized to provide power systems in a number of discrete power levels for applications of a more general nature than heretofore. For example, the SNAP-21 [10- to 20-W(e) systems] generators may be used for various deep-sea applications, navigational aids, seismological stations, oceanographic research, or hydrophone amplifiers. The SNAP-23 [25- to 100-W(e)] is planned for surface applications, such as offshore navigational aids, unmanned seismological stations, microwave repeater stations, aircraft landing systems, and remote communications systems.[2,6]

The United Kingdom Atomic Energy Authority (UKAEA) is designing and building thermoelectric generators using <100-W $^{90}SrTiO_3$ for applications similar to those of the AEC generators. Four to six devices have been completed in the RIPPLE (*R*adio*i*sotope *P*owered *P*rolonged *L*ife *E*quipment) program, and several more are in various stages of design or construction (see Table 1). Isotopes,* Aerojet–General Corp., and Nuclear Materials & Equipment Corp. (NUMEC) are now marketing commercial generators using ^{90}Sr heat sources, and the AEC is supplying the sources for them as well as for the RIPPLE generators. Fuel forms are being fabricated at ORNL from ~8 MCi of ^{90}Sr that was separated by Hanford between 1961 and 1965.

OPERATION OF RADIOISOTOPE-POWERED ELECTRIC GENERATORS

Long life and minimum maintenance have been the major incentives for the development of radioisotopic power sources for marine and terrestrial uses and for the U. S. space program. The power provided by suitable radioisotope sources can be as high as several watts per cubic centimeter of source material, with a useful life of tens of years. The kinetic energy of the electromagnetic or charged-particle products of radioisotope decay is transformed either directly into electricity or indirectly, through a preliminary conversion, to heat. Most of the devices developed to date use a thermoelectric generator to convert the heat to electricity.

Radioisotope-powered thermoelectric conversion systems have demonstrated reliability and maintenance-free lives of >40,000 hr and power levels up to 100 W(e). Their initial capital cost per electrical watt is high, but their cost on a watt-hour basis compares favorably with that for other energy sources for applications in remote and inaccessible areas. Even in relatively accessible regions, the cost of transporting alternative energy supplies can be of considerable significance, and in such inaccessible regions as the North or South Pole, desert, or jungle the additional costs of transporting materials and of servicing the systems increase tremendously.

SEPARATION PROCESSES

Strontium-90 is one of five long-lived products formed in relatively high yield in reactors from the fission of uranium and recovered separately. The other abundant fission products having half-lives greater than 6 months are ^{99}Tc, ^{137}Cs, ^{144}Ce, and ^{147}Pm. An attractive goal, envisioned for many years, has been an integrated separations process that would separate each fission product in turn and result in a reduced amount of radioactive waste. The goal remains incompletely realized, but most of these fission products now can be purified in megacurie quantity.[9]

Several processes—$PbSO_4$-carrier precipitation, ion exchange, and solvent extraction—accomplished the large-scale purification of ^{90}Sr at Hanford in the interval 1961–1965. No similar scale production has been carried out since that time. The Hanford Waste Management Program unit of the Atlantic Richfield Hanford Company now separates a crude ^{90}Sr product for storage.

Purity Requirements[10]

Because of design requirements for thermoelectric generators, stringent demands are made on the ^{90}Sr recovery process. Gamma emitters have to be removed to a level insignificant in comparison with the associated bremsstrahlung radiation in order to take advantage of the lower biological shielding requirements of ^{90}Sr–^{90}Y beta emitters. Thus the specifications for the purified product require that each gram of ^{90}Sr contain <0.0015 Ci of gamma emitters with energies >2 MeV, <0.015 Ci in the 1- to 2-MeV range, and

*In 1968 Martin Company sold its nuclear activities to Teledyne, Inc., whose subsidiary, Isotopes, Palo Alto, Calif., will take over the Martin Company contracts and programs in this area.

<0.15 Ci in the 0.2- to 1-MeV range. This specification corresponds to separation factors of the order of 10^4 to 10^5 from ^{144}Ce, ^{95}Zr–^{95}Nb, ^{106}Ru, and most other gamma-emitting fission products.

A high degree of purification from inert contaminants is also required so that the specific heat-generating rate of $^{90}SrTiO_3$ will equal or exceed* the design criterion of the generators (0.5 W/cm^3 in 1961, >0.8 W/cm^3 since 1967). The contaminants must be less than 25 wt.% of the total cation weight, and the ^{90}Sr content must be greater than 36% of the total cation weight.

The waste solutions resulting from the recovery of uranium from spent reactor fuel elements, which constituted the starting material for the recovery of fission products, were highly acidic and contained large quantities of such inorganic ions as sulfate, nitrate, iron(III), sodium, aluminum, and chromium (see Table 2 for the composition of Purex 1WW waste). Decontamination factors† of up to 2000 for iron, 700 for lead, 400 for aluminum and chromium, and 10 for calcium and barium were required at the time of the SNAP-7 program.

Strontium-90 is produced as a fission product during reactor operation along with ^{89}Sr, which has a half-life of 50.5 days, and other strontium isotopes (including the stable isotopes ^{86}Sr and ^{88}Sr). Yttrium-90, the decay daughter in secular equilibrium with ^{90}Sr, emits a very-high-energy beta particle. The intense high-energy beta activities of ^{89}Sr and ^{90}Y, as well as the softer beta activity of ^{90}Sr, result in high-energy bremsstrahlung radiation for which heavy shielding is required. Unless the strontium has aged sufficiently, the 50.5-day ^{89}Sr also contributes a substantial fraction of the heat of the isotopic mixture.

The radioisotopic properties of fission-product strontium are[11] given in Table 3. A year of aging is necessary for a heat source with only a minor contribution from ^{89}Sr; otherwise the source will show a high initial decrease in heat output, characteristic of the short-lived ^{89}Sr. Removal of ^{89}Sr stabilizes the generator temperatures to match the narrow operating range of PbTe thermocouples.

Hanford $PbSO_4$-Carrier Precipitation Process. The $PbSO_4$-carrier precipitation process was developed and used at Hanford to recover megacurie amounts of crude ^{90}Sr for final purification.[12,13] However, the process has not been used since the 1961–1965 large-scale recovery programs. Initially the process feed was concentrated Purex 1WW waste (Table 2), which contained essentially all the fission products and relatively large amounts of contaminant metals and sulfate in ~4*M* HNO_3. Feed preparation with Purex acid waste (PAW§) includes a centrifugation step to remove solids (primarily silica and sulfates), which carry appreciable quantities of fission products.

A typical flow sheet of this recovery process, which has had several variations, is shown in Fig. 1. Cerium and other rare earths are precipitated as the sodium–rare-earth double sulfates along with the strontium by adjusting the sulfate concentration to ~1*M* and the *p*H

Table 2 Typical Composition of Purex 1WW Waste

Component	Concentration, moles/liter	
	1961–1965	October 1969‡
H	4	6
SO_4	1.0	0.6
NO_3	4.5	7.7
Na	0.6	0.7
Fe	0.5	0.35
Al	0.1	0.3
Cr	0.01	0.035
Ni	0.01	0.02
UO_2	0.005	0.01
Sr	0.002	0.0015
Cs	0.003	0.002
Sm	0.006	0.006
Ce	0.003	0.0025
Ru	0.003	0.002
Ca	0.005	0.002
Zr		0.008
SiO_2		0.1
PO_4		0.015
Be		0.05
Cu		0.06
La		0.0015
Li		0.001
Mg		0.04
Mn		0.0065
Mo		0.0035
Ba		0.0025
Nd		0.0025
Solids	10%	10%

‡Private communication, D. E. Larson, Atlantic Richfield Hanford Company, Richland, Wash.

*Present sources are 0.85 W/cm^3.

†Ratio of initial to final weight of contaminant per gram of ^{90}Sr.

§The PAW is similar to Purex 1WW but contains only ~1*M* HNO_3.

XUM

Table 3 Radioisotopic Properties of Fission-Product Strontium

Isotope	Half-life	Beta energy (max.), MeV	Gamma energy, MeV
^{89}Sr	50.5 days	1.463	0.91 (0.009%)
^{90}Sr	28.5 years	0.546	None
^{90}Y	64.0 hr	2.28	None

of the solution to 1 to 2. Lead nitrate is added to carry strontium sulfate, and an iron complexing agent (such as tartrate or hydroxyacetic acid) is added to avoid precipitation of ferric sulfate. The precipitated sulfates are metathesized with a mixture of NaOH and Na_2CO_3 to remove lead (by conversion to soluble plumbite) and to convert the strontium, along with cerium and the other rare earths, to acid-soluble carbonates. These carbonates are dissolved in nitric acid and cerium and

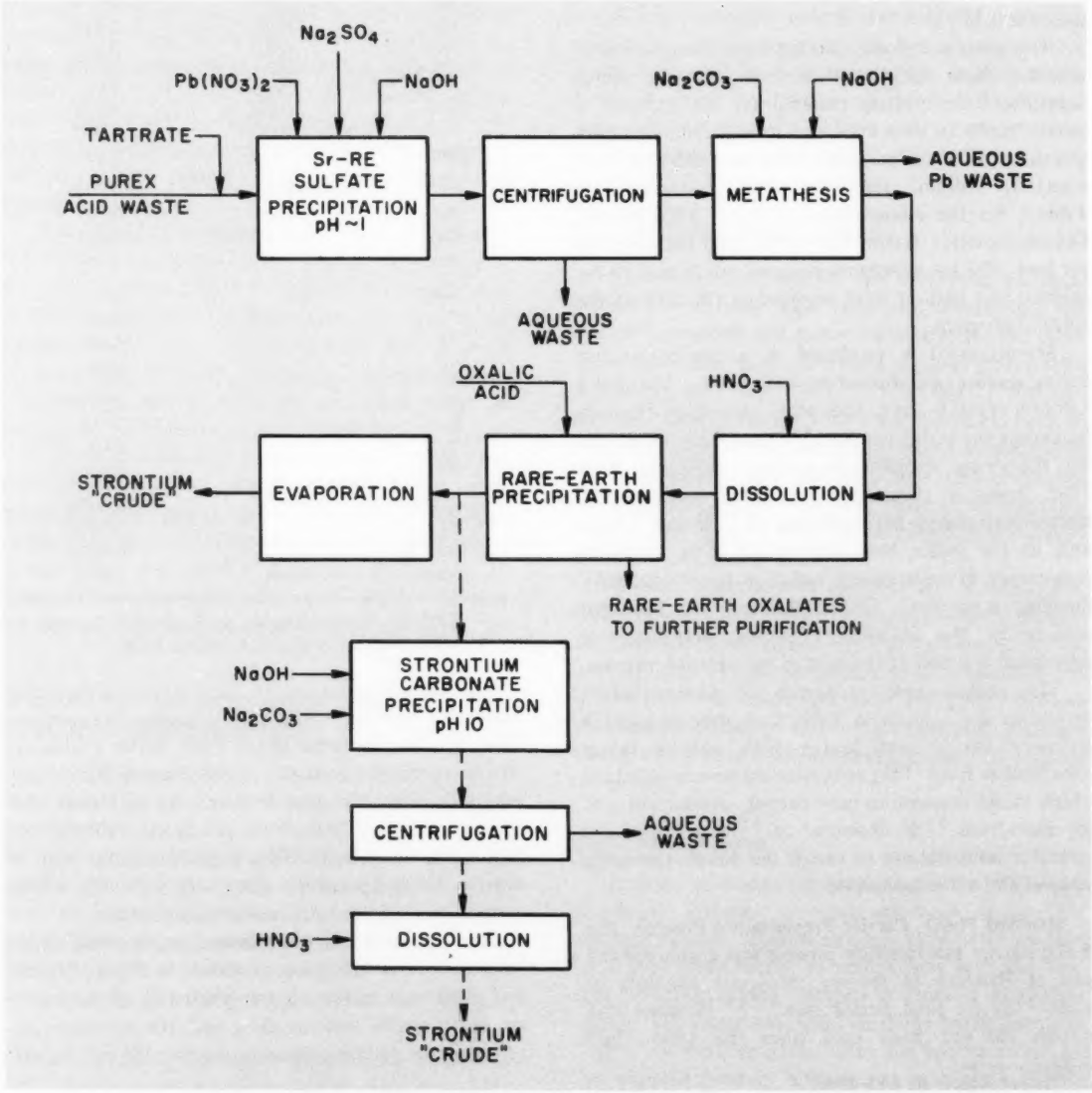


Fig. 1 Strontium and rare-earth recovery from Purex waste by $PbSO_4$-carrier precipitation.

XUM

other rare earths are separated from strontium by precipitating them as the oxalates, leaving the strontium in solution.

Strontium can be concentrated by evaporation or by precipitating strontium carbonate and dissolving it in nitric acid. The crude solution is then ready for ion-exchange or solvent-extraction processing.

In a series of pilot-plant runs at Hanford to test the waste-management process[14] with nonradioactive strontium, recovery of strontium was ~85%, with overall strontium decontamination factors of 17 to 460 from iron, 90 to 100 from aluminum, 370 to 500 from manganese, 55 to 90 from nickel, 7 to 60 from calcium, 28 to 125 from magnesium, and 1 to 8 from lead. No oxalate precipitation was performed in the waste-management process.

Hanford Solvent Extraction Process. To a large extent the solvent extraction process was based on modifications and further development of the solvent extraction technology developed at ORNL using di(2-ethylhexyl)phosphoric acid (HDEHP) for recovery and purification of strontium and rare earths from Purex waste.[15,16] Many process variations and flow sheets have been devised at Hanford for different process objectives and for handling different waste compositions, but only the production process is described here.

The first Hanford solvent extraction process for fission-product separations[10,13,17] was developed specifically for use in the Hot Semiworks Pilot Plant to purify ^{90}Sr for SNAP-7 program requirements. Feed is prepared from crude strontium product solution recovered by the $PbSO_4$-carrier precipitation process by adding acetate for buffering, sodium hydroxide for adjusting acidity, a small amount of Na_2SO_4 for barium removal, and diethylenetriaminepentaacetic acid (DTPA) for complexing the extraneous metals. This complexant suppresses extraction of iron, lead, and certain fission products, such as zirconium–niobium and ruthenium. In the process flow sheet (Fig. 2), strontium, calcium, residual mixed rare earths,

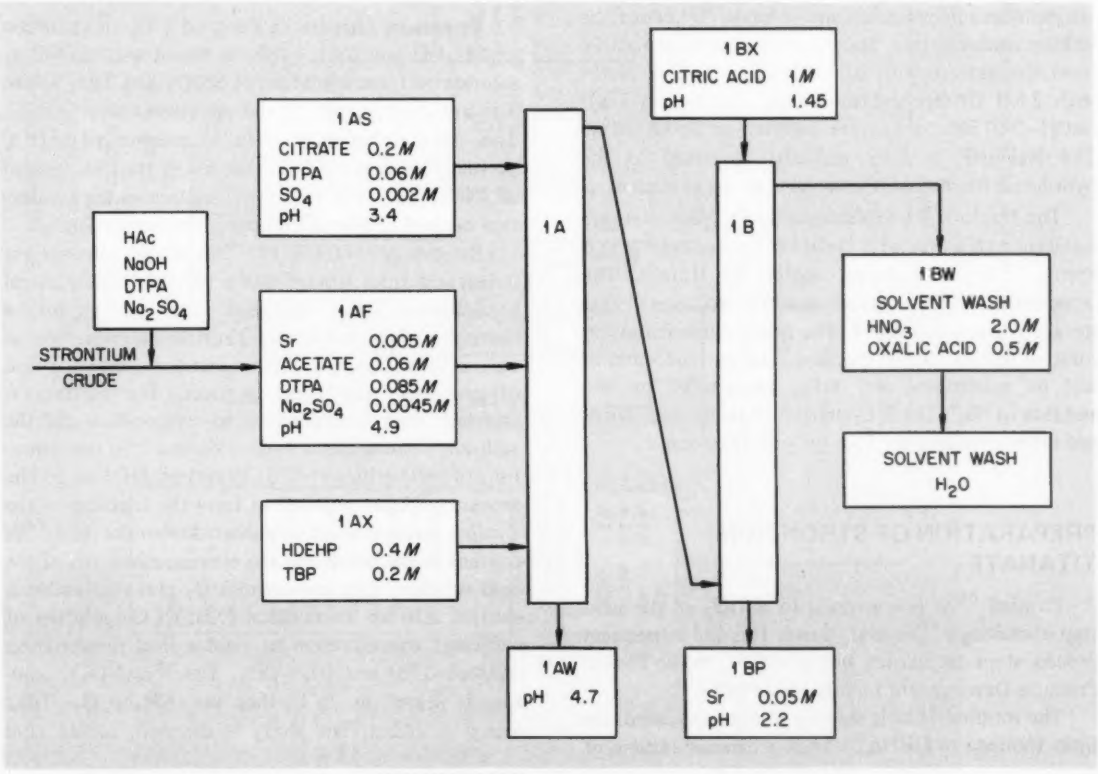


Fig. 2 Strontium recovery using one cycle of solvent extraction.[19]

and some sodium are coextracted with 0.4*M* HDEHP and 0.2*M* tributyl phosphate (TBP) in hydrocarbon diluent.* A large portion of the extracted sodium is scrubbed from the solvent at *p*H 3.4 to 4.7 with sodium citrate–DTPA–sodium sulfate solution. Strontium is stripped selectively in a second contactor with 1*M* citric acid at *p*H 1.5 to 2.1 to separate it from calcium and rare earths. The product is concentrated, and the citrate is destroyed by oxidation with a boiling HNO_3–H_2O_2 solution. The product may be further purified by either an ion-exchange cycle or a second solvent extraction cycle.

Improved Hanford Solvent Extraction Process. Hanford has devised processes for direct treatment of low-acid Purex wastes by solvent extraction to remove strontium and rare earths.[18] A typical flow sheet[19] is shown in Fig. 3. The aqueous feed is complexed with citric acid and adjusted with NaOH to a *p*H of 4.5 to 5. Strontium and rare earths are coextracted at 40 to 50°C with HDEHP (partially in the sodium salt form) and TBP in a hydrocarbon diluent, and the solvent is scrubbed with hydroxyacetic acid–trisodium hydroxyethylethylenediaminetriacetate solution to reduce the sodium concentration. Strontium is stripped selectively from the extract with 0.03*M* HNO_3, the rare earths with 2.5*M* HNO_3, and the waste metals with 1.8*M* NaOH–0.075*M* Na tartrate solution at about 50°C. The NaDEHP is then partially converted to the hydrogen form before it is recycled to the extractor.

The Hanford Waste Management Program now uses a solvent extraction with NaDEHP to concentrate and purify ^{90}Sr from Purex wastes for storage. The composition of a typical product solution[20] for storage is given in Table 4. The stored crude strontium solution will be further purified. The purified solution will be neutralized and SrF_2 precipitated by the addition of NaF. The SrF_2 slurry will be filtered, dried, and doubly encapsulated for underwater storage.

PREPARATION OF STRONTIUM TITANATE

Purified ^{90}Sr is converted to $SrTiO_3$ in the next step of making a ^{90}Sr heat source. This and subsequent process steps are carried out at ORNL in the Fission Products Development Laboratory (FPDL).[21]

The purified ^{90}Sr is shipped as the solid carbonate from Hanford to ORNL.[22,23] A schematic outline of the process steps for converting purified $SrCO_3$ to encapsulated $SrTiO_3$ is shown in Fig. 4.

Present Procedures for Compound Preparation

Feed Material. The first step in preparing the feed material is to unload the Hanford casks by drawing water through the cask under steam-jet vacuum and slurrying the $^{90}SrCO_3$ into a collection tank. After most of the $^{90}SrCO_3$ has been removed from the cask, the cask is rinsed with 2*M* nitric acid; the acid is added to the collection tank to convert the $^{90}SrCO_3$ slurry to $^{90}Sr(NO_3)_2$ solution. The amount of acid used is calculated so as to yield a final solution ~1*M* in HNO_3 for storage. The cask is dried, sealed, leak-tested, decontaminated, and then shipped back to Hanford.

The $^{90}Sr(NO_3)_2$ solution is sampled and stored at the FPDL in stainless-steel water-cooled tanks, which can hold 6 MCi of $^{90}Sr(NO_3)_2$ feed solution. The radiochemical purity of this material is >99.9% (exclusive of ^{89}Sr, the amount of which is dependent on the age of the material); its major inert contaminant is calcium. Table 5 shows a typical feed analysis.

Strontium Titanate. A slurry of TiO_2 in a solution of NH_4OH and $(NH_4)_2CO_3$ is mixed with $Sr(NO_3)_2$ solution to form a mixture of $SrCO_3$ and TiO_2 solids. The solids are filtered off and calcined to form $SrTiO_3$. This method has been used to prepare all $SrTiO_3$ powder produced at FPDL. The use of Na_2CO_3 instead of $(NH_4)_2CO_3$ was the only variation in the production method of Martin Company, Nuclear Division.†

Batches of ~40 kCi of $^{90}Sr(NO_3)_2$ solution are transferred from storage into a 150-liter stainless-steel precipitation vessel equipped with an agitator, a heating–cooling jacket, and a bottom-discharge line, as well as the standard instrumentation, sampling and off-gas lines, and other services. The solution is sampled; then it is adjusted by evaporation and the addition of ammonium hydroxide to a ^{90}Sr concentration of ~10 g/liter (~750 Ci/liter) at *p*H 3 to 5. The amount of TiO_2 required to form the titanates of the alkaline earths present is calculated from the total ^{90}Sr content in the batch and the elemental analysis of the feed solution. This amount of TiO_2 plus a 5% excess is slurried into an ammoniacal $(NH_4)_2CO_3$ solution of sufficient concentration to yield a final precipitation solution 0.7*M* in $(NH_4)_2CO_3$. The $^{90}Sr(NO_3)_2$ solution is heated to 70°C; then the $(NH_4)_2CO_3$–TiO_2 slurry is added. The slurry is digested, cooled, and

*Amsco, Shell spray base, or normal paraffin hydrocarbon.

†Martin Company, Nuclear Division, prepared SNAP-7B and SNAP-7F heat sources at its Quehanna pilot plant.[24]

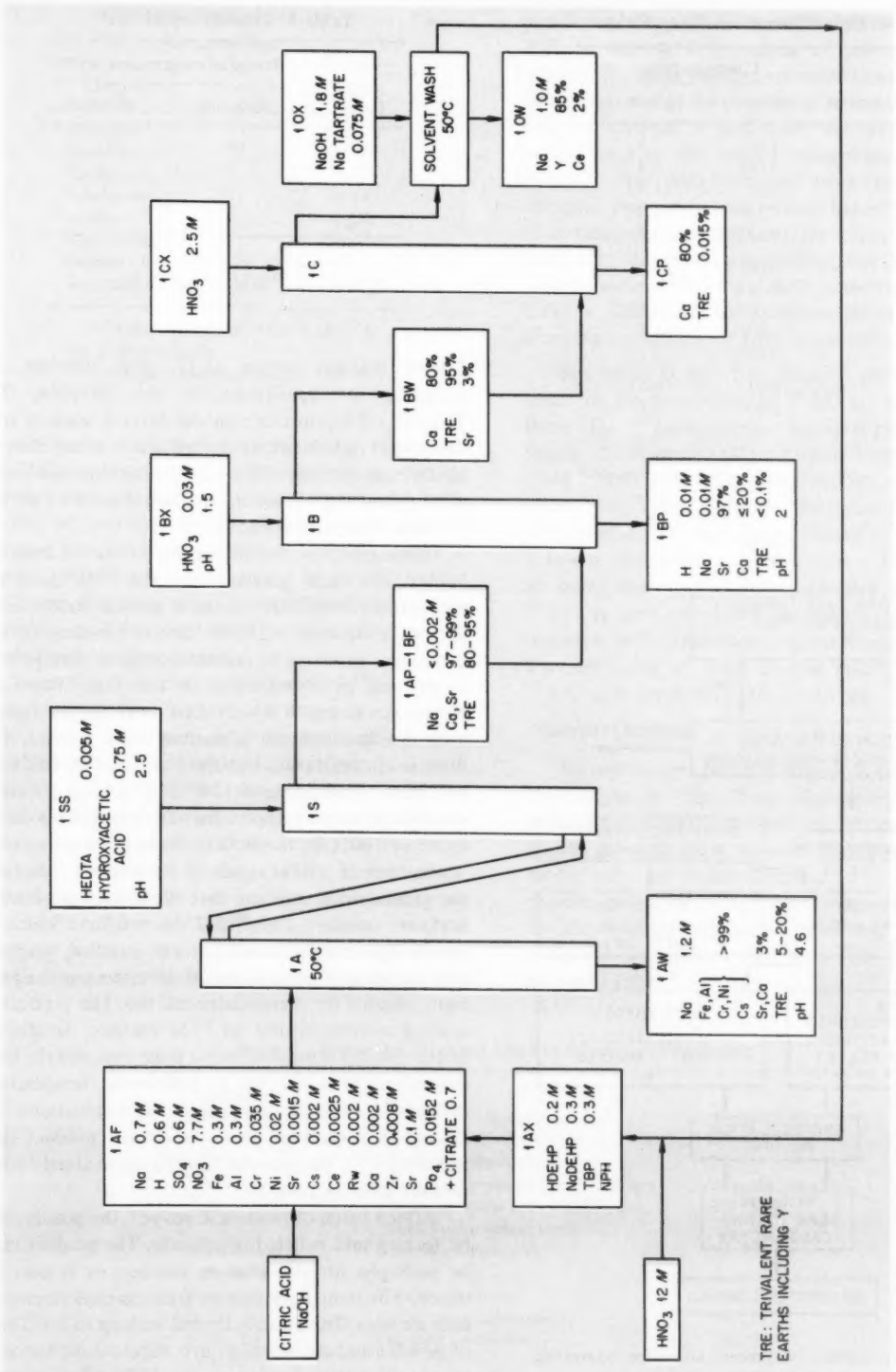


Fig. 3 Recovery of strontium and rare earths from Purex PAW.

Table 4 Crude Strontium Composition

Constituent	Concentration	
	Molarity	g/liter
H	2.85	2.8
Sr	0.096	8.4
Na	0.51	11.7
Ca	0.158	6.3
Mg	0.183	4.5
Ba	0.0016	0.22
Mn	0.201	11.0
Ni	0.0024	0.14
Al	0.041	1.1
Cr	0.0055	0.29
Fe	0.011	0.61
Pb	0.010	2.1
^{144}Ce–Pr	(232 Ci/liter)	
^{90}Sr	(705 Ci/liter)	

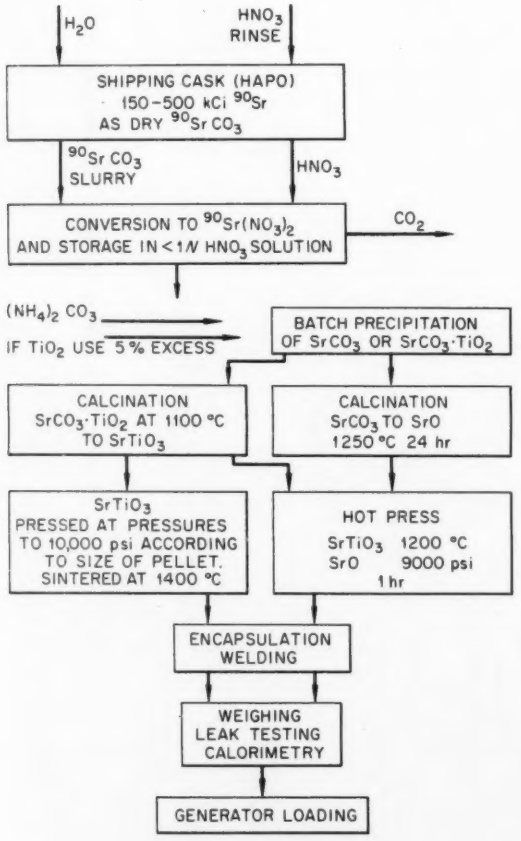


Fig. 4 Schematic outline of process steps for converting purified $SrCO_3$ to encapsulated $SrTiO_3$ and SrO.

Table 5 Feed Composition*

Cation	Range of composition, wt.%	
	Maximum	Minimum
Sr	97	92
Ca	5	2
Ba	2	0.5
Mg	2	0

*One gram of ^{90}Sr will produce 0.0232 g of ^{90}Zr after 1 year's decay.

filtered through porous Al_2O_3 filter thimbles. No difficulty is experienced in the filtration. The $^{90}SrCO_3$–TiO_2 mixture on the filter is washed with dilute $(NH_4)_2CO_3$ solution; then it is dried by drawing air through the filter. The Al_2O_3 filter thimbles have a total volume of ~1800 ml, and the volume of 40 kCi of dried precipitate is ~1500 ml.

After the filter thimble has been removed from the system, the heat generated by the ^{90}Sr dries the precipitate completely. Since a normal batch has a thermal output of ~250 W, careful handling of the material is necessary to prevent damage to manipulator boots and other materials in the cell. When the precipitate is dry, it is stirred to break up any lumps; then the filter thimble is inserted into a furnace. The furnace temperature is increased at a rate of 100°C/hr to a final temperature of 1100°C. This temperature is maintained for 4 hr; then, after the furnace is cooled at a rate of 100°C/hr to <400°C, the thimble is removed.

Batches of ~10 kCi each of the calcined $^{90}SrTiO_3$ are ground in a stainless-steel blender to produce a uniform powder. The $^{90}SrTiO_3$ product, which is usually light brown in color, can be handled, weighed, and transferred using standard laboratory-size equipment adapted for manipulator-cell use. The product is assayed calorimetrically for ^{90}Sr content. An aliquot of the powder is weighed into a brass cup, and the heat output is measured by a differential temperature calorimeter. Several calorimetric determinations are run on each powder batch to ensure product uniformity.[25,26] The powder has the approximate composition given in Table 6.

After a batch of product is assayed, the powder can be formed into pellets immediately. The product may be packaged for shipment as powder, or it may be stored. For temporary storage stainless-steel screw-top cans are used. The cans are loaded with up to 7-kCi lots of powder and are stored in dry water-cooled tubes in an in-cell storage facility at the FPDL. This storage

Table 6 Typical $SrTiO_3$ Composition

Component	Wt.%
Strontium	36*
Titanium	28
Calcium	3
Zirconium	5
Barium	0.5
Magnesium	0.5
Oxygen	26
Iron, lead, carbon	Traces†

*Product contains ~30 Ci of ^{90}Sr per gram of powder.
†Traces are <1% of total.

system has a capacity of approximately 2 MCi of $^{90}SrTiO_3$ powder. For long-term storage, welded stainless-steel containers are used, each of which holds 3.3 kCi of powder. These containers also serve as shipping cans for large amounts of $^{90}SrTiO_3$; larger or smaller shipments can be made in similar welded containers of various sizes. A circumferential groove is provided in these containers so that they can be opened with a tubing cutter.

From the feed analysis the ratio of ^{90}Sr to total strontium, calcium, barium, and magnesium is calculated, and from these data the heat output of a particular batch can be related to its chemical composition. When the composition of a product is outside the range desired, the powder may be blended mechanically with other products, which vary in the other direction, to produce products of the desired grade. Several product batches of varying compositions may be combined in one blending operation. Standard blending practices are carried out in a stainless-steel blender. Successful blendings have been made by using powders in which the TiO_2 was deficient by as much as 30% or was 40% in excess of the stoichiometric amount, but most powders are much closer in composition. When one of the powders is deficient in TiO_2, the blended material is recalcined. No differences have been found in the pellet-forming characteristics of powders that were prepared from the same feed solution, even when one powder batch was the result of a blending operation and the other was a single batch that did not require blending. Hot-pressed pellets can be made with TiO_2-to-SrO ratios that vary from TiO_2 in 30% excess of stoichiometric to pure SrO by changing the amount of TiO_2 in the slurry.

Strontium Oxide. The chemical processing operations for the preparation of ^{90}SrO are very similar to those for $^{90}SrTiO_3$. The precipitation procedures simply eliminate the TiO_2 addition. Calcination of the dried $^{90}SrCO_3$ to ^{90}SrO is carried out at 1250°C for 24 hr. The ^{90}SrO products are converted to pellets immediately after calcination. During the short period between calcination and pelletization (while samples are being assayed, dies are being loaded, etc.), the bulk ^{90}SrO is kept at ~550°C to minimize combination reactions with atmospheric water and carbon dioxide. The possibility of these adverse reactions eliminates ^{90}SrO as an inventory form for storage.

Analytical Methods

Process control depends largely on calorimeters for the analysis of ^{90}Sr. Those calorimeters designed and constructed at FPDL measure the rate of heat production of the radioactive material. Two general types are used—one for solid samples,[25,26] consisting of powder, pellet, or encapsulated source, and the other for solutions of radioactive strontium.[27] Additional analytical methods employed in ^{90}Sr processing are shown in Table 7.

Table 7 Analytical Methods Used in Strontium Processing

Quantity to be found	Method	References
$SrTiO_3$	Fusion and dissolution	28
^{90}Sr	Gross beta by proportional counters	29*a*, 30*a*, 31
^{89}Sr	Yttrium removal with D2EHPA, then Sr-absorption study	29*b*, 30*b*
Other fission products	Gamma spectrometry	32, 33
Mass analysis	Mass spectrometry	29*d*, 29*e*
Ca, Ba, Sr	Flame spectrophotometry	29*c*, 34
Ti, Zr, Mg, Fe, Pb	Emission spectroscopy	30*c*, 35

XUM

FUEL FABRICATION

In the fuel-fabrication process, powdered $SrTiO_3$ or SrO is converted into pellets suitable for encapsulation. Design of the source, shield, and generator requires reproducible physical properties in the pellets, especially accurate dimensions. Ideal physical characteristics of a source include high density, high thermal conductivity, high melting point, high thermal stability, and good mechanical properties.

Several methods for fabricating materials (especially polycrystalline ceramics) into dense pellets are described in the literature.[36-39] In general, all these methods consist in the application of heat and/or pressure over a period of time. The heat and pressure may be applied simultaneously or in sequence. Forming methods can be divided into three groups:

1. Cold forming usually consists of the application of pressure to the material. Cold-forming methods include slip casting, extrusion, injection molding, die pressing, isostatic pressing, and vibratory compaction. The compacts produced by pressing may be subsequently heated to yield higher densities.

2. Hot forming consists in the simultaneous application of heat and pressure. Hot forming methods are hot pressing by uniaxial pressure, biaxial pressure, or isostatic pressure with gas or liquid medium or with semifluid "sand"; and hot swaging.

3. Melt casting consists in the application of heat, but no pressure.

The application of pressure in any hot- or cold-forming method sometimes involves a high-energy-rate procedure, such as pneumatic impaction, explosion, or electrical discharge.

All the methods of cold forming, hot forming, and melt casting were evaluated for use with strontium fuel forms. The following methods were tested experimentally: die pressing–heat treating, isostatic pressing–heat treating, uniaxial hot pressing, biaxial hot pressing, and melt casting. The methods of isostatic hot pressing and pneumatic impaction at high temperatures were evaluated by visiting and consulting with other workers; other methods were evaluated by a literature search.

From this study, several general conclusions were drawn with reference to the forming of strontium fuels. With the exception of isostatic pressing (followed by firing), which requires expensive and complicated equipment, the cold-forming methods have two primary advantages over the hot-pressing method for $SrTiO_3$: they are simple to carry out in a hot cell and they are inexpensive. However, the densities achieved with cold pressing are low, and the reproducibility and dimensional control are poor. These factors are difficult to regulate even with closely controlled and reproducible powders. For strontium fuels the control of particle size (a critical parameter in cold-forming methods) is not feasible. For isostatically pressed samples, if the pressure exceeds the strength of the particles, high unfired (green) densities can be obtained. The small additional shrinkage on firing allows good control of dimensions.

The hot-forming method (except isostatic hot pressing) has two distinct advantages over the cold-forming or melt-casting methods: improved dimensional accuracy of the compact formed and adaptability of the method to a wide variety of materials. The hot-forming method also has the advantage that two materials can be allowed to react to produce the desired compound as the compact is being formed (reactive hot pressing). Isostatic hot pressing gives poor dimensional control unless the powder is prepressed to densities greater than 85% of theoretical; this is not possible with the ^{90}Sr power fuels investigated. In addition, isostatic hot pressing is difficult and expensive for hot-cell operation.

Uniaxial or biaxial hot pressing can be accomplished readily in a hot cell with moderate equipment cost.

Melt-casting methods are more applicable to materials that melt below 1200°C than with current strontium fuels having high melting points (Sr_2TiO_4, 1860°C; $SrTiO_3$, 2040°C; and SrO, ~2400°C). The melt-casting method was not considered competitive with hot pressing. In general, the densities obtained by casting are low owing to high void volumes and to the formation of casting "pipes."

Strontium Titanate

Both cold-pressing and sintering and hot-pressing techniques have been used for forming multikilocurie $SrTiO_3$ pellets, but the cold-pressing and sintering method failed to produce SrO pellets of adequate density. Since 1966, most of the $SrTiO_3$ and SrO pellets have been formed with the hot-pressing technique. A hot press for radioactive material in a hot cell was designed and fabricated[40] for use at FPDL, as well as a small hot press for laboratory or glove-box operation[41] (Figs. 5 and 6).

The initial hot-pressing tests on $SrTiO_3$ were done on nonradioactive titanate in equipment at the Oak Ridge Y-12 Plant Development Division. These tests indicated that essentially theoretical densities could be

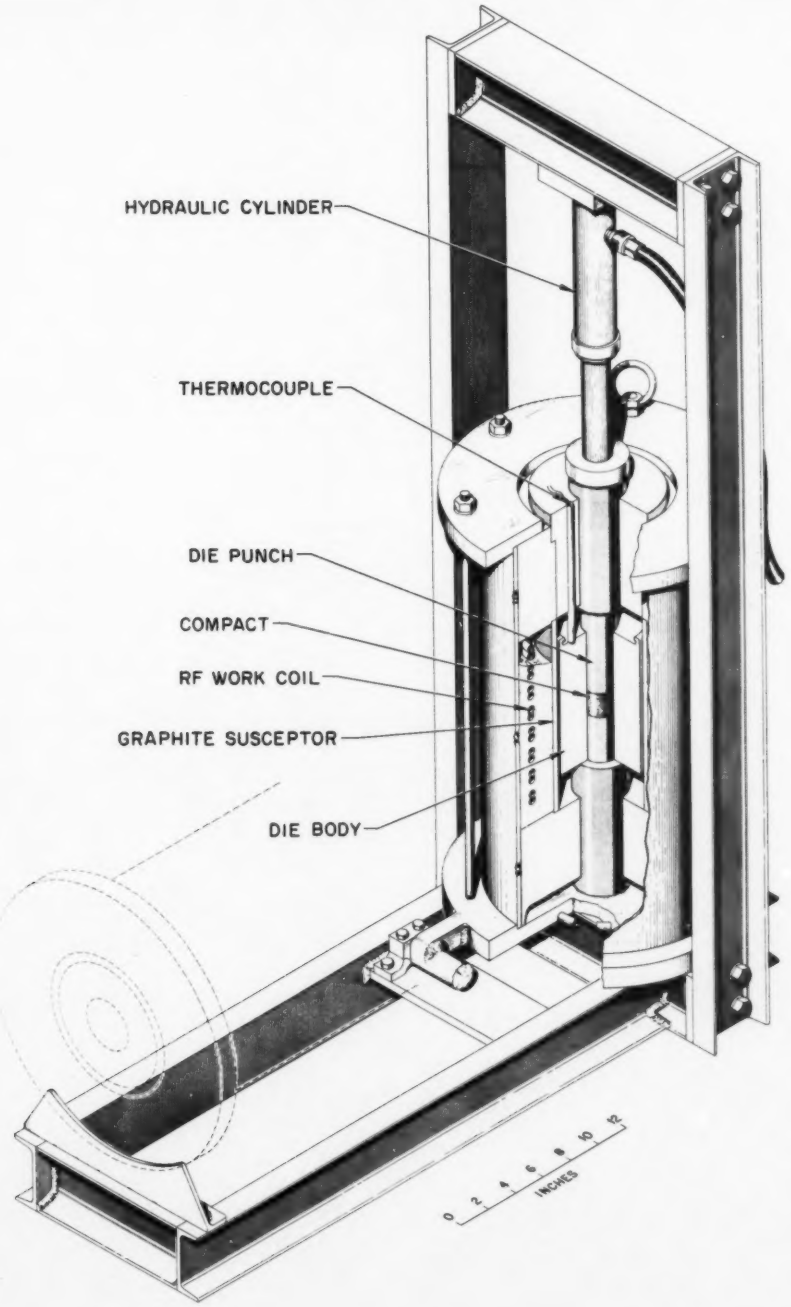


Fig. 5 Hot press for remote operation.

XUM

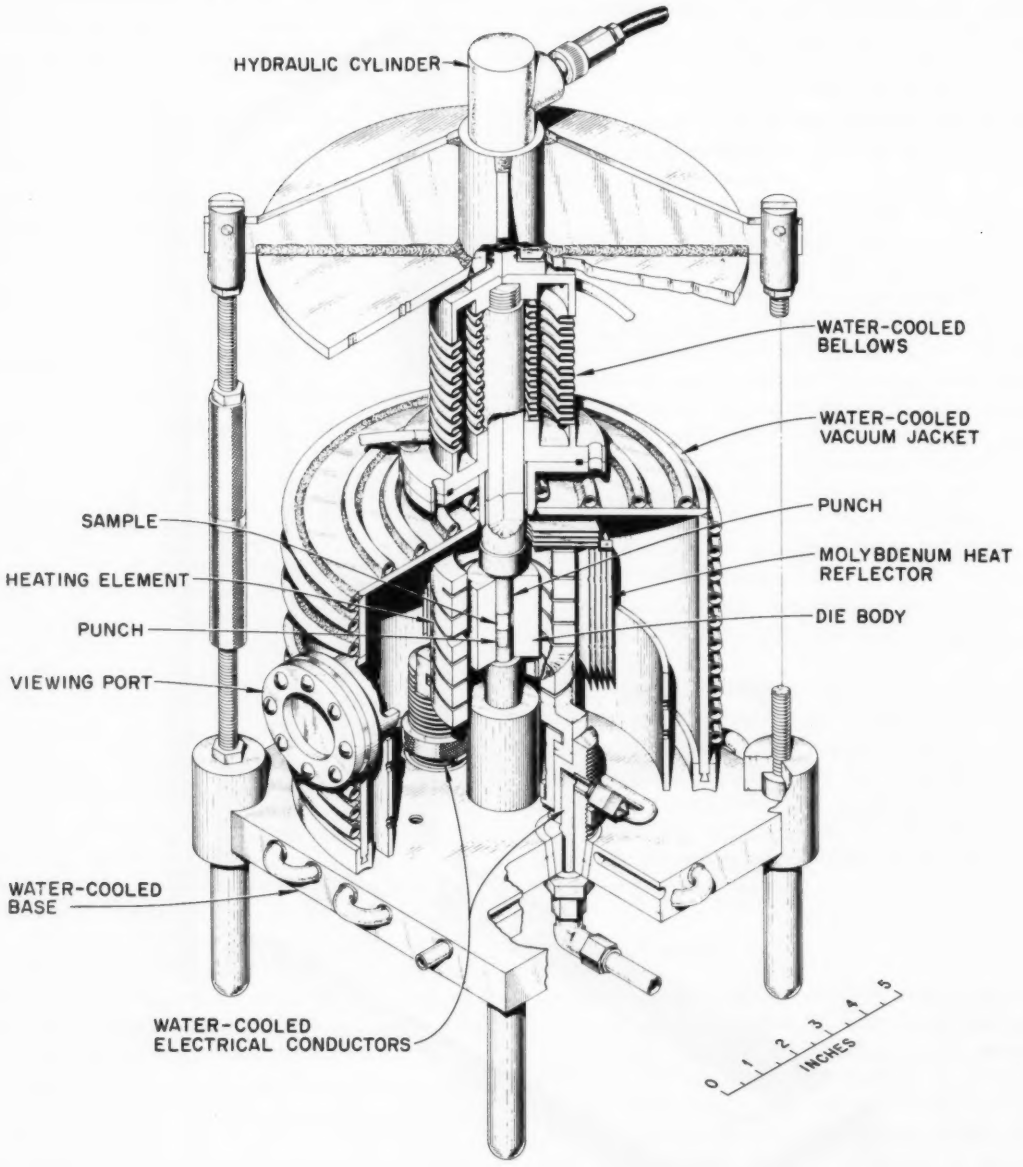


Fig. 6 Miniature hot press.

obtained on 2-in.-diameter compacts by hot pressing at 1300°C for 30 min with a pressure of 2500 psi. The densities obtained were 5.00 g/cm^3 (calculated density = 5.05). The $SrTiO_3$ was freshly precipitated and calcined powder. Full pressure was applied to the press at the start of the heating cycle.

Subsequent tests over a wide range of conditions and with various powders led to several conclusions. The factors that control the densification are discussed separately.

Although a hot-pressing procedure is relatively insensitive to the history of the powder, it has been observed that slightly higher densities for given pressing conditions can be obtained with freshly prepared powder. The next highest densities are obtained with aged $SrTiO_3$ powder, and the lowest, with highly sintered or previously hot-pressed and crushed material.

In general, the higher the temperature at which the pellet is pressed, the higher the density (up to 100% of theoretical); or, the shorter the time, the lower the pressure to obtain a given density. The temperature should never exceed 1450°C. At this temperature the pellet rapidly decreases in density with extensive fragmentation. This is presumed to be due to a solid–solid phase transition at that temperature. At 1350°C, densification of all powders tested was sufficiently rapid for pressing times of less than 1 hr to be required.

The pressure that can be applied to a die is limited by the die geometry and the strength of the graphite. A pressure of 4 thousand psi is adequate for a pressing time of less than 1 hr. Die designs for 4 thousand psi on 4-in.-diameter compacts are considered practicable. Pressures in excess of 4 thousand psi, when strength considerations permit, will reduce the pressing time required. Sintering of $SrTiO_3$ powder occurs at an appreciable rate at 900 to 1000°C. For this reason the pressing should be started at 900°C.

Strontium titanate pellets of 2-in. diameter were hot pressed to essentially theoretical density under the following conditions:

Maximum temperature	1300°C
Pressure	1000 psi at 1000°C, increasing to 3000 psi at 1300°C
Time at maximum temperature	1 hr

The theoretical density of pure $SrTiO_3$ is 5.11 g/cm^3. The calculated density of fission-product $^{90}SrTiO_3$ with the magnesium, calcium, and barium impurities is 5.05 g/cm^3.

Future application of $SrTiO_3$ may require sources with diameters of up to 5 in. Strontium titanate treated at high temperatures (1200 to 1400°C, the temperatures for hot pressing) in a neutral or reducing atmosphere undergoes a reduction in the oxygen stoichiometry. Under reducing conditions, $SrTiO_3$ has the composition $SrTiO_{2.99}$ (Ref. 41). Pellets of reduced $SrTiO_3$ are jet black. If the pellets are of high density and reduced, they are severely strained and subject to cracking. Annealing cannot be accomplished at <2000°C. Pellets of $SrTiO_3$ 3 in. in diameter have been hot pressed from both active and inactive $SrTiO_3$. All 3-in.-diameter radioactive pellets have exhibited extensive cracking due to thermal gradients. Pellets of inactive $SrTiO_3$ are highly sensitive to thermal shock; they also frequently crack. To help maintain the integrity of the pellets, several conditions of the preparation and fabrication procedure were studied to determine their influence on cracking. The only significant result is the observation that low-density pellets (<4.0 g/cm^3) are much less likely to crack.

Two methods were tested successfully on 1-in.-diameter pellets. These were (1) inclusion of randomly oriented 5-mil wire, ¼ in. long, in the pellets and (2) jacketing the pellet with platinum wire gauze. The wire gauze is mechanically held in the surface of the pellet. A later technique was developed using nickel-wire screens incorporated in the horizontal plane. This technique has been used on pellets as large as 4 in. in diameter (300 W) with good success. The cost savings relative to platinum are significant.

In the hot-pressing procedure, the powder is first prepressed; then the pellet charge is added incrementally to the die body holding the bottom punch. After the addition of each 20% increment, nickel screen is added, and the powder is pressed at 2000 psi with a stainless-steel punch. After all the charge and screens have been added, the top punch is inserted.

The loaded die body is removed from the prepressing assembly and inserted into the hot press; the guide collar and drive punch are then inserted on top of the die body to align the system. Thermocouples are inserted through penetrations in the guide collar so that they contact the die body. The hot press is then raised to the vertical position, and a set of brass shims and mica insulators are placed between the graphite drive punch and the hydraulic press ram. The hot press is heated by means of a radio-frequency motor generator to 1100°C, then a pressure of 3000 psi is imposed. While the pressure is still on the system, the

XUM

hot-press temperature is raised to 1300°C; the pressure and temperature are maintained for ½ hr. The pressure is then relieved, and the hot press is cooled to ~300°C. During all periods in which the hot press is above 300°C, a flow of inert gas is maintained through the hot-press cavity. In some cases an inert atmosphere is maintained in the entire cell. Alternative furnaces use resistance heaters as well as radio-frequency heaters.

The die body is removed from the hot press and placed in the prepressing assembly. A steel drive punch extrudes the punch and pellet, which are allowed to drop into a handling tray. The completed pellets are weighed and measured. A ring gage with an inside diameter identical to the capsule is used to check diameter and roundness of the pellet.

The capsules are degreased and wrapped in plastic for insertion into the cell. Pellets are inserted into the capsules, and the press-fit lid is fitted. The flat plate and the taper on the cap force the cap evenly into the capsule, thus forming an even weld area. The loaded capsules are finally welded, leak-tested, and assayed calorimetrically.

Handling tools used in the cell are made of stainless steel. During pellet fabrication and capsule loading, no water is used in the cell, and no organic materials are allowed to contact the fuel. Since the die bodies are made of graphite, some graphite will adhere to the surfaces of the pellets; this can be seen as discoloration on the pellets. Pellets are brushed with stainless-steel brushes, but no other cleaning is done on them. Completed pellets are stored on aluminum oxide trays, and pellets and capsules are handled with stainless-steel tools. During welding the capsules are held in a brass chill block. Cotton swabs are used to clean weld areas, and paper smears are used to detect contamination. Decontamination solutions used for final capsule cleaning are detergents, weak nitric acid, and water.

Strontium Oxide

Experience indicated that most of the densification occurs at less than 800°C. Tests were made with full pressure applied to the die punch, beginning at room temperature and increasing to 1200°C. If the temperature is increased at a rate of 100°C/hr from 750 to 850°C, full densification is attained at 850°C. However, if the temperature is raised to above 1200°C before pressure is applied, the density does not exceed 4.4 g/cm^3 even if the temperature is increased to 1600°C. These tests were done in a vacuum hot press with a capacity for up to 1-in.-diameter pellets. The results suggest that either a large change occurs in the surface energy of the powder at about 850°C or a sintering aid that exists as an impurity in the SrO powder is destroyed at that temperature. The latter is believed to be more likely. Small amounts of either $Sr(OH)_2$ or $SrCO_3$ could be present and account for the low-temperature sintering. As a matter of precaution, the pellets are heated to 1200°C following densification to calcine any $Sr(OH)_2$ or $SrCO_3$ that might be present.

Estimates from thermodynamic data predict that SrO will not react with carbon to produce strontium carbide at temperatures of less than ~1500°C. Since the final procedure does not require a temperature in excess of 1200°C, tests were made on hot pressing SrO directly in graphite dies instead of molybdenum-lined dies. The SrO pellets were analyzed for strontium carbide, and none was found. No problems of sticking of the SrO to the graphite die and punch material were encountered. A platinum liner may be used to provide protection from moisture when pellets are fabricated in air.

When pellets are formed by hot pressing in an inert atmosphere, small bubbles of the gas at the pressing pressure can be trapped in the pellet. The gas may subsequently diffuse into the void volume and cause an increase in the pressure inside the capsule. With vacuum hot pressing, this possibility is avoided, and the pellets have a higher density.

Three 202-W ^{90}SrO heat sources were prepared by hot pressing. Four batches of ~35 kCi of $^{90}SrCO_3$ each were prepared, and the dried $^{90}SrCO_3$ powder was calcined in air at 1200°C for a minimum of 24 hr. The pellets were of excellent appearance with no change in appearance or dimensions after 10 days.

SOURCE ENCAPSULATION AND TESTING

The final step in the preparation of a heat source is to encapsulate the pellets in a suitable metal to hold the pellets in the desired location and to prevent absolutely the spread of radioactive material to the environment. The resulting capsules must be leak-free, thermally and structurally stable, and capable of delivering the designed quantity of heat to the generator elements. They also must be resistant to chemical attack by the radioactive fuel and by the environments encountered during source fabrication and normal use and in credible accidents after source fabrication.

Source-fabrication studies at ORNL include consideration of the heat flow and the temperature

XUM

distribution within the source. The designers of a generator generally require that a specified heat flux be delivered at a given temperature. These requirements must be met without creating excessive temperature anywhere in the source. High temperature reduces the strength of structural materials and increases corrosion rates and can also cause melting or movement of the radioactive fuel by volatilization. Extremely high temperatures could occur in heat sources of poor design.

Large temperature drops may develop at interfaces between layers of encapsulating material and at the interface between the fuel and the capsule. The number of interfaces should be minimized, and calculations must show that the maximum possible temperature is not excessive.

Large temperature differences can exist between the surface and the interior of the radioactive fuel (with or without a diluent or matrix material) in heat sources. These gradients are created by the flow of heat, generated throughout the radioactive material, to the surface. Very high internal temperatures can result.

At the present state of generator development, the maximum temperature designated for the surface of the strontium titanate capsules is <1000°C. In SNAP-7 generators it is ~500°C. The maximum internal temperature can be lowered by the configuration of the capsule, by dilution with a good conductor (cermets), or by the introduction of metallic laminars into the $SrTiO_3$.

Welding of ^{90}Sr Containers[42]

Inert-Gas Tungsten-Arc Welding. The primary fuel container for present-day ^{90}Sr sources is a Hastelloy alloy C capsule, welded by the inert-gas tungsten-arc (TIG) process. The main reasons for the choice of Hastelloy alloy C as the primary container are its excellent seawater corrosion resistance and satisfactory weldability. However, in one case a source prepared for a Si–Ge thermoelectric converter was encapsulated in a TZM (99% Mo, 0.5% Ti, 0.1% Zr) inner capsule and a Hastelloy alloy X outer container. Other than for the common choice of Hastelloy alloy C as an encapsulating material, there has been no standardization in capsule-weld design. The weld-joint design and the weld-penetration requirements have been set largely by the particular application rather than by limitations in source-fabrication technology.

Since ^{90}Sr is not an alpha emitter, no gas builds up in the capsule, and a full-penetration pressure-vessel type weld is not generally required. Thus the characteristic of $^{90}SrTiO_3$ containers has been a partial penetration weld produced by the TIG process. In most cases the weld-joint design has been some modification of the edge-type of "trepanned" design (Fig. 7). This design is employed for several reasons. First, it is a relatively low-restraint joint which minimizes any tendency toward cracking due to shrinkage as the weld cools. This is particularly important if the cap and capsule body are fairly massive. In this case, a partial penetration weld in a plain butt-type joint would almost invariably crack due to the restraining effect of the relatively cool and therefore strong material surrounding the weak weld metal as it attempts to contract during cooling. This tendency toward cracking is aggravated by the presence of the unwelded portion of the joint which acts as a built-in crack starter at the root of the weld.

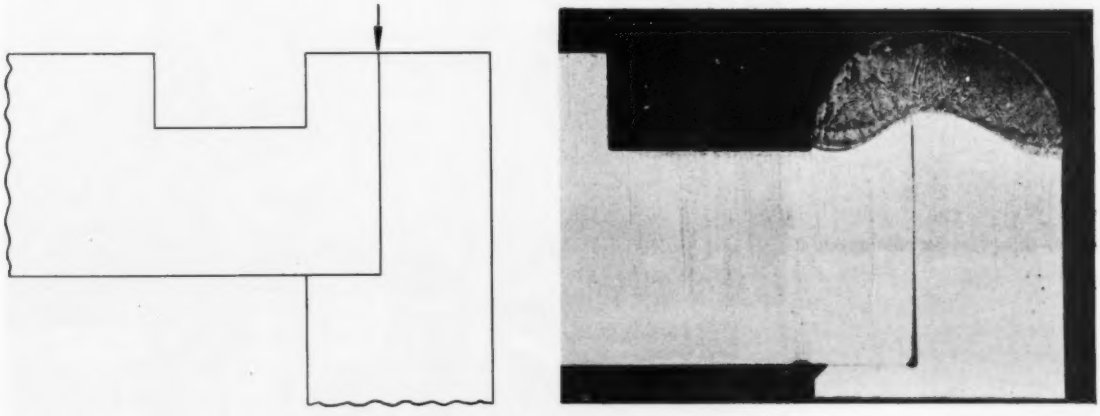


Fig. 7 Edge-type weld joint.

XUM

The second reason for use of this joint design is that the shape of the weld bead can be observed easily. From this, the experienced welder can judge the amount of weld penetration being obtained, which, in turn, allows him to control the process during the operation.

The third reason for preference of the edge-type weld joint design is that no filler metal is required. Compared with a flat butt-type joint, the edge-type joint can be thought of as providing its own filler metal. Open groove-type joints that require filler metal are not generally desirable for this application because the added complexity of the wire feeding equipment and wire handling adds to the difficulty of welding in a hot cell and requires additional space. The chief reason for considering such a weld would be the need for additional weld-metal penetration. However, if a weld of great depth is to be obtained by one of these methods, the weld must also be quite wide. Thus a tremendous amount of weld metal would be required on a comparatively small weldment (the capsule), and the result would likely be unacceptable distortion.

When the welding gas must be of known composition, purity, and pressure, a closed-chamber welder is used, which has provisions for evacuating the system, introducing the gas, measuring the temperature and pressure, remotely positioning the electrode, viewing the welding operations, and cooling the source. (A typical welding assembly is shown in Fig. 8.)

If the welding atmosphere need not be closely controlled, open TIG welding can be used. Most remote welding techniques employ a fixed electrode with the source rotated in a chuck. Sources with very low radiation and many alpha emitters can be welded with a hand-held torch in a glove box.

In welding these sources by the conventional TIG process, it has been found useful to have the welder maintain complete control over the welding current. This is very desirable if, for some reason, an inaccurate estimate was made of the preheating effect of the fuel pellets. However, as greater assurances of weld penetration and overall quality are required because of a developed welding procedure that adequately takes into account the effect of capsule preheat, operator

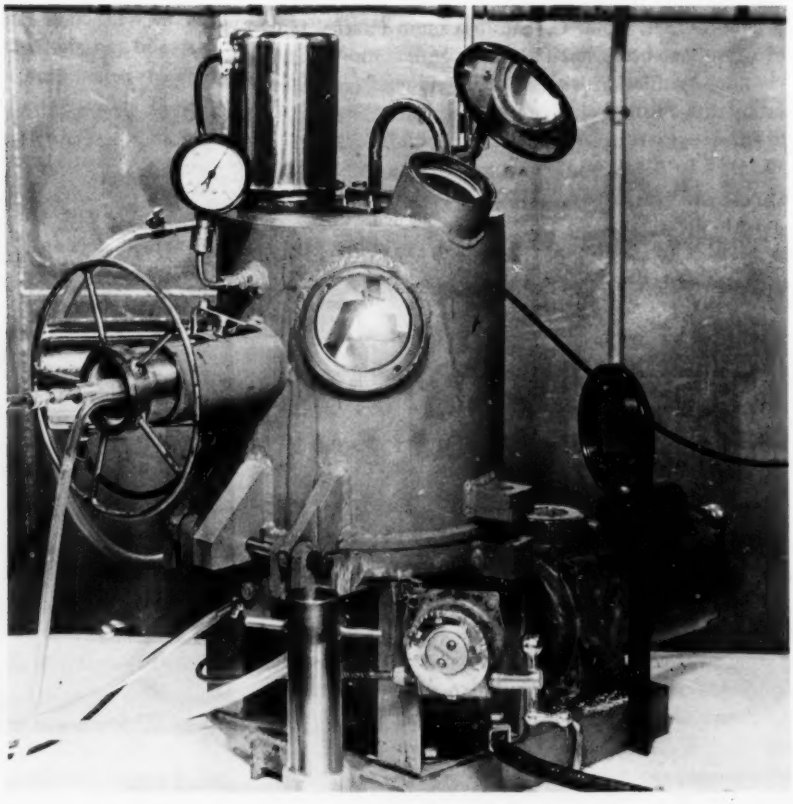


Fig. 8 Closed remote welding cell.

"control" can become an uncontrolled variable. Thus the trend is toward a welding procedure developed and carried out semiautomatically on a program-controlled welding power supply. This method gives greater assurance of weld quality.

In addition to the leak-testing procedures, other inspection procedures are used to better assure the quality of the welded capsule. These include the inspection of "quality-assurance samples," one of which is welded immediately prior to the fueled capsule or capsules and another immediately after. These sample capsule welds are normally of the same joint configuration as the actual capsule but do not always mock up the fueled capsule completely. For instance, the sample may not be of full height nor be completely machined.

The examination of these samples usually includes dye- or fluorescent-penetrant inspection of the weld area for cracks or pits and a leak test. The samples are subsequently sectioned for metallographic examination of the welds. This is done to verify the weld penetration and quality at either two sections of weld 180° apart or four sections 90° apart. This procedure can give reasonable assurance of the fueled-capsule weld quality if the sample welding adequately mocks up the fueled capsule.

Electron-Beam Welding. If welds are needed with penetration significantly greater than that which can be obtained by the techniques described above, electron-beam welding is adaptable to hot-cell use. Electron-beam welding is preferred over adding filler wire to conventional welds because of the drawbacks cited earlier for filler-wire additions and because the electron-beam process is very amenable to remote operations. Figure 9 shows the electron-beam welding equipment; the chamber, vacuum system, and electron-beam gun (left side of photograph) would be positioned in-cell, and the control console and power supply would be positioned out-of-cell. A typical weld on a Hastelloy alloy C capsule is shown in Fig. 10 joining a 0.300-in.-thick cap to a 0.250-in.-thick capsule wall. The depth and continuity of the electron-beam weld are inspected by a pulse–echo ultrasonic method. The method shows defects in the weld of the order of the size of the reflected sound wavelength.

Leak Testing

Radioactive materials for use as radiation or heat sources must be encapsulated in a manner that will prevent the release of radioactivity during normal operations or under potential accident conditions.

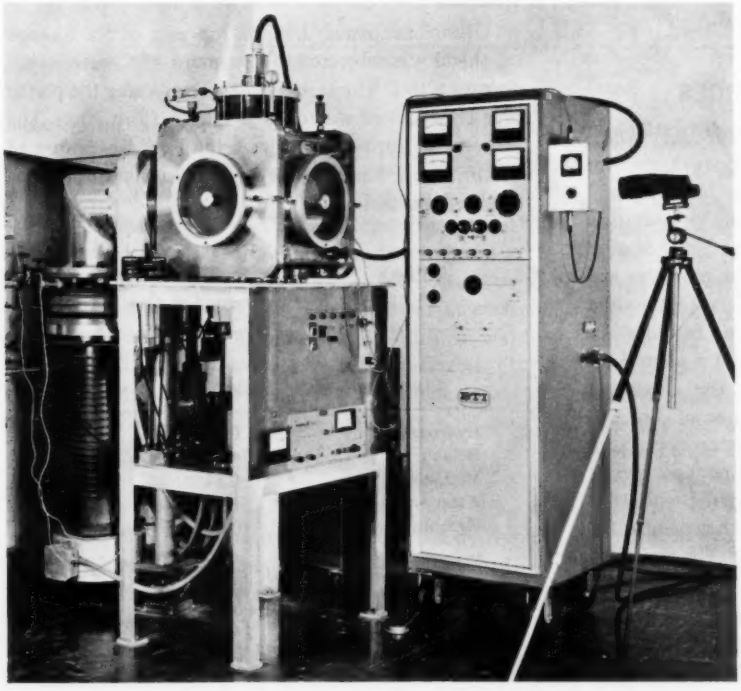


Fig. 9 Electron-beam welding equipment.

XUM

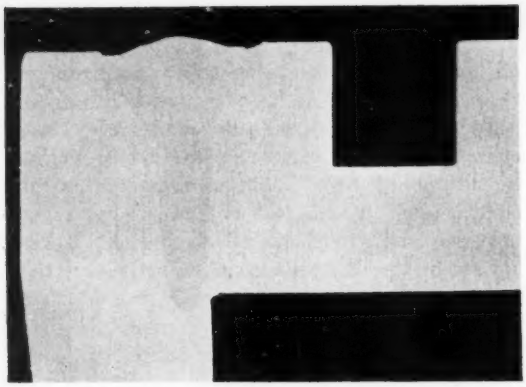


Fig. 10 Electron-beam weld.

Most sources are encapsulated in welded metal containers, and an important requirement is a demonstration that the welded closure is free from significant leaks. Methods of leak testing at FPDL are usually limited to those procedures which can be performed by remote means using manipulator-operated equipment. These methods involve immersion in some type of liquid;[43] however, if immersion methods are unsuitable because the source has a high thermal output or the encapsulating method is incompatible with the test liquid, a ^{85}Kr leak-test procedure is used.

EXAMINATION OF USED SOURCES

The SNAP-7A $^{90}SrTiO_3$-fueled generator, which had been operating in a navigational buoy for 5½ years, was received in 1967 for defueling and inspection.[44] This generator had been in operation since December 1961 at the U. S. Coast Guard Station at Curtis Bay, Md. The outer case of the generator was unchanged except for a thin film of rust deposited evenly over the surface. Radiation readings of 20 mR/hr beta-gamma were measured at a point 5 in. from the top of the shielding case. The maximum power output measured was 4.2 W(e) as of Apr. 20, 1967 [original design, 10 W(e)]. The internal pressure of the generator as determined during periodic servicing was 18.5 psia in April 1967, compared with 15.9 psia in March 1964. Two samples of the generator fill gas were analyzed by mass spectrometry. The results of the analysis are given in Table 8.

The weld on the generator casing cover was ground off. and the generator casing was separated from the biological shield, which was a large uranium cup completely encased in ¼-in.-thick Hastelloy alloy C plate. The generator with the casing was lifted out of the shield and examined. There was no visible evidence that the Hastelloy alloy C generator casing had been amalgamated by the mercury heat-transfer medium in which the casing had floated for over 5 years. The mercury was removed from inside the biological shield, and the Hastelloy alloy C shield liner was examined visually. There was no evidence of amalgamation.

The generator was defueled in one of the FPDL cells on Apr. 25, 1967, and the fuel capsules were inspected. The insulation block was found to be broken, but no other physical damage to the generator was noted. No radioactive contamination was detected during the removal of the top plate. The maximum radiation reading at the top of the biological shield was 750 mR/hr. When the defueled generator was removed from the cell, a smear test of the outside lip read 1200 dis/min, and all inside smears read <500 dis/min. No ^{90}Sr was detected on any of the smears.

Microscopic examination of a core section of the biological shield revealed that the solder (50% Pb–50% Sn) used to bond the uranium and Hastelloy alloy C to form a heat-transfer path had only ~1-mil penetration on the side exposed to mercury and on the side exposed to the marine atmosphere. The solder was well bonded to the uranium, but there was no bond to the Hastelloy alloy C.

The nickel-plated uranium top plug of the biological shield was subjected to a standard AEC water-vapor corrosion test. The test consists in exposing the plated plug to saturated water vapor at 92.5°C for 20 hr. The test was performed five times for a total exposure of 100 hr. There was no evidence of corrosion or penetration of the nickel plate.

Table 8 Mass Spectrometric Analysis of SNAP-7A Generator Fill Gas

Compound	Amount, vol.%	
	Sample 1	Sample 2
Hydrogen	0.04	0.02
Helium	74.5	75.3
Methane	0.14	0.01
Water	1.45	1.17
Hydrocarbons	<0.01	<0.02
Nitrogen and carbon monoxide	0.51	0.42
Oxygen	0.28	0.16
Argon	23.1	22.9
Carbon dioxide	<0.004	0.02

Each SNAP-7A fuel capsule contained six $^{90}SrTiO_3$ pellets and a number of Hastelloy alloy C spacers encapsulated in a welded Hastelloy alloy C capsule. The capsules were essentially identical in fuel content and arrangement. All the $^{90}SrTiO_3$ used in these sources was prepared during August 1961 from the same $^{90}Sr(NO_3)_2$ feed material. Portions of three batches of $^{90}SrTiO_3$ with power concentrations of 0.231, 0.233, and 0.219 W/g were used. The calculated compositions of these fuel batches, based on the original feed analysis and decay to August 1967, are given in Table 9. All the pellets used in the SNAP-7A sources were made by the cold-pressing and sintering method. Two $^{90}SrTiO_3$ batches that were deficient in titanium dioxide yielded pellets with an average power density of 0.73 W/cm^3; the 7% excess TiO_2 material yielded pellets with an average power density of 0.92 W/cm^3. All pellets were intact when loaded into the capsules.

Heat Output

The water-jacketed calorimeter was used to determine the heat outputs of the four capsules. The calculated heat contents (based on original loading data and corrected for decay from September 1961) are compared below with those experimentally determined (on Apr. 27, 1967):

Heat output, W	
Calculated	Experimental
54.9	56.6
54.6	56.6
55.0	56.7
54.8	56.6
219.3	226.5

The 3% difference in total heat output is probably due to overcorrection for ^{89}Sr contribution.

Table 9 Calculated Composition of $^{90}SrTiO_3$ Fuel

Batch No.	Constituent, wt.%						Power concentration, W/g	Ratio	
	Sr	Ca	Ba	Zr	Ti	O		SrO/TiO_2	$^{90}Sr/Sr$
17	38.1	2.9	0.2	6.0	26.2	26.6	0.199	0.95	0.47
18	38.5	2.9	0.2	6.0	25.9	26.5	0.201	0.93	0.47
19	36.1	2.7	0.2	5.7	27.9	27.4	0.189	1.07	0.47

Capsule Inspection

Each of the four capsules was removed from the generator and given a smear test; no significant contamination was detected. All the capsules appeared to be in excellent condition; all were discolored to a dull gray. No defects in the weld areas could be detected by visual inspection. The diameter of each capsule was measured by passing it through 1- and 4-in.-long ring gages having an inside diameter of 1.900 in. (originally 1.872 in.). The maximum height measured 5.210 in. (originally 5.198 in.).

Leak Tests

The capsules were individually leak tested by the hot-water air-bubble method; no leaks were detected. Two capsules at a time were leak tested with ^{85}Kr. The ^{85}Kr leak tests revealed no leaks (limit of detection, 1×10^{-7} cm^3/sec). The capsules originally had been welded in helium at 30 psig.

Inside Capsule and Pellet Examination

Figure 11 shows the unopened capsules with the weld made in the hot cell. Each capsule was opened by cutting through the wall at a point 1 cm below the end welded in the hot cell. The capsule was inverted, and the capsule body was lifted off to expose the spacers and the fuel. Spacers and pellets were marked for identification as they were removed from the capsule.

After the pellets and spacers had been removed, the capsules were brushed to remove any loose material. A 2-cm-high ring section was cut from the center of the capsule body. The other (shop) weld was cut off the capsule 1 cm from the end. The two weld sections, center section, and selected spacers from each capsule were transferred to the High Radiation Level Examination Laboratory (HRLEL) for metallurgical inspection.

There was no visible evidence of mechanical damage or chemical attack on the inside capsule surfaces or on the spacers. The fuel pellets and spacers were easily removed from the capsules. No residual fuel could be

XUM

Fig. 11 SNAP-7A capsules showing hot-cell welds.

seen on the disassembled capsule parts. The maximum radiation reading on the package, with specimens shielded only by the thin metal walls of the package, was 300 mR/hr; this reading indicates that relatively little ^{90}Sr was retained in the specimens.

Of the 24 pellets (Fig. 12), 15 were completely intact, 7 were cracked across the diameter, 1 was slightly chipped, and 1 was broken into several pieces. One-half of the broken pellet was intact, but the other half was broken up (this pellet had initially cracked diametrically, as had the 7 other pellets). There was no detectable change in the color of the pellets.

No significant dimensional changes in the pellets could be noted. The total weight of fuel material recovered was 1127 g, of which 1123 g was as pellets (or individual pieces) and 4 g as loose powder, compared with an original loading of 1124 g.

Metallurgical Examination of Capsules

Visual examination of the four disassembled SNAP-7A capsules (with the aid of a remote stereomicroscope) disclosed no evidence of gross incompatibility or weld defects.

The components of capsule No. 4 were selected for metallographic examination. Examined were a typical section through the bottom and upper closure welds, a section taken through the wall of the capsule at about midlength, and a section through several spacers that had been placed between the $^{90}SrTiO_3$ pellets.

Examination of the closure weld revealed a minimum penetration of 0.085 in. A minimum penetration of 0.180 in. was measured on the bottom weld, and there was no evidence of any microstructural defects.

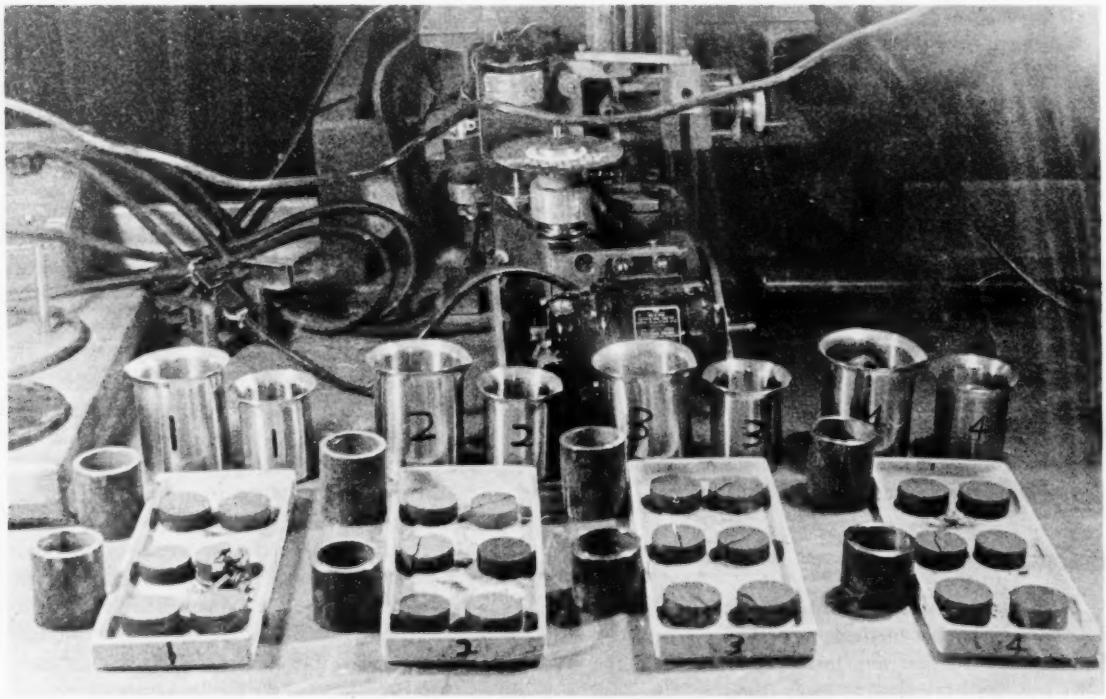


Fig. 12 SNAP-7A fuel capsules and pellets after opening.

XUM

Metallographic examination of the capsule wall disclosed no evidence of incompatibility; the inner and outer surface regions appeared to be identical. Examination of the spacers yielded similar results.

Summary

There was no serious deterioration of these sources during their 5½-year life. The distribution of the broken pellets according to fuel batch is interesting: 6 of the 9 high-density titanate-excess pellets broke, but only 2 of the 15 low-density titanate-deficient pellets broke (neglecting the pellet that was only chipped). Similar effects have been noted previously both with cold-pressed and sintered pellets and, more markedly, with hot-pressed pellets.

PROPERTIES OF STRONTIUM FUEL FORMS

Physical and Chemical Properties

Chemical forms in addition to $SrTiO_3$ and SrO possess desirable properties for power-source applications. Some important physical and chemical properties of forms considered for use as power sources are compared in Table 10. The full report contains more data and references all values.

Biological Tolerances for ^{90}Sr

The maximum permissible concentrations of ^{90}Sr internal and external to humans are shown in Table 11.

Table 10 Physical and Chemical Properties of Strontium Fuel Forms[11]

Property	Sr metal	$SrTiO_3$	SrO	SrF_2	Sr_2TiO_4
Specific power					
100% Sr (55% ^{90}Sr)					
W/g	0.513	0.247	0.435	0.360	0.315
Ci/g	76.5	36.8	64.8	53.7	47.0
95% Sr–5% Ca, Mg, Ba					
W/g	0.487	0.235	0.411	0.336	0.294
Ci/g	72.7	34.1	61.2	50.0	43.8
Density, g/cm^3					
100% Sr (55% ^{90}Sr),	2.6	5.11	4.975	4.29	4.99
95% Sr–5% Ca, Mg, Ba	2.5	5.03	4.63	4.20	4.93
Power density, W/cm^3					
Theoretical	1.33	1.26	2.17	1.54	1.57
Actual or estimated		1.0	1.6	(1.4)*	(1.4)*
Melting point, °C	772	2040	2457	1463	1860
Thermal conductivity at 500°C, 10^3 cal/(cm)(sec)(°C)	250	9.2	5.5	4.2	7.6
Specific heat (500°C), cal/(g)(°C)	0.0719 (at 25°C)	0.157	0.124	0.167	0.142
Coefficient of thermal expansion/°C x 10^5	2.0	1.21†	1.13†	1.63 (at 25°C) 2.44 (at 30°C)	1.17†
Solubility in H_2O, moles/liter x 10^4	Reacts vigorously			9	1.7
Leach rate					
SrO: 1.49 g/(cm^2)(day)(H_2O at 4.4 cm/min)					
$SrTiO_3$: $\ln R = -0.5235 \ln t - 2.5987$					
R = leach rate, mg/(cm^2)(day)					
t = time, days					

*95% ^{90}Sr, 90% theoretical density.
†0 to 1400°C.

Table 11 Maximum Permissible Body Burdens and Maximum Permissible Concentrations for ^{90}Sr in Air and in Water for Occupational Exposure

Organ of reference (critical organ in italics)		Max. permissible burden in total body (q), μCi	Maximum permissible concentrations, $\mu Ci/cm^3$			
			For 40-hr week		For 168-hr week	
			Water	Air	Water	Air
(Sol)	*Bone*	*2*	4×10^{-6}	3×10^{-10}	10^{-6}	10^{-10}
	Total Body	*20*	10^{-5}	9×10^{-10}	4×10^{-6}	3×10^{-10}
	GI (LLI)*		10^{-3}	3×10^{-7}	5×10^{-4}	10^{-7}
(Insol)	*Lung*			5×10^{-9}		2×10^{-9}
	*GI (LLI)**		10^{-3}	2×10^{-7}	4×10^{-4}	6×10^{-8}

*GI, gastrointestinal tract; LLI, lower large intestine.

Compatibility Studies

Fuel-form compatibilities with various container materials are summarized in Table 12.

A number of reactions were dependent on time and temperature; for example, Haynes alloy No. 25 with strontium metal showed no attack at 1000°C up to 1000 hr but fell into the major reaction classification after 5000 and 10,000 hr at 1000°C. This indicates that Haynes alloy No. 25 should probably not be considered for use with strontium metal at temperatures >1000°C and times >5000 hr.

After exposure of 2036 hr at 925°C to inactive liquid strontium metal, it was found that molybdenum and stainless steel 321 showed good compatibility with liquid strontium metal; that wrought iron and Haynes alloy No. 25 were worthy of further study; and that Hastelloy alloy C, Hastelloy alloy N, Hastelloy alloy X, and titanium had dissolved and were incompatible with strontium metal.

Table 12 Compatibilities of Inactive Strontium Compound with Container Materials

Source material and exposure	Container material*								
	Superalloys				Refractory metals				
	Hastelloy alloy X	Haynes alloy No. 25	Ni-o-nel	N-155	Mo	Nb	Ta	W	TZM
Strontium metal (Sr)									
1000°C, 1000 hr	SR	NR	SR	MR	NR		SR	NR	NR
1000°C, 5000 hr		MR		MR			SR	NR	
1000°C, 10,000 hr		MR	MR	MR	NR		SR	SR	
Strontium oxide (SrO)									
1000°C, 1000 hr	SR		SR	SR	NR	NR	SR	SR	
1850°C, 168 hr					SR	MR	SR	SR	
Strontium–9% beryllium oxide (SrO–9% BeO)									
1000°C, 1000 hr		MR	MR	SR	NR			NR	NR
Strontium fluoride (SrF_2)									
1000°C, 1000 hr	SR	SR	SR	SR	NR		SR	SR	
Strontium disilicide ($SrSi_2$)									
1000°C, 168 hr	DR	DR	DR	DR	DR		DR	DR	DR
Strontium titanate ($SrTiO_3$)									
1000°C, 1000 hr	SR	SR	SR	SR	NR		NR	NR	NR
1850°C, 1000 hr					NR	SR	SR	NR	MR

*NR, Negligible or no reaction (compatible); DR, Destructive reaction (incompatible); SR, Slight reaction; MR, Major reaction.

REFERENCES

1. W. R. Corliss and D. G. Harvey, *Radioisotope Power Generation,* Prentice-Hall, Inc., Englewood Cliffs, N. J., 1964.
2. J. E. Carden, International Study of Terrestrial Applications of Radioisotopic Power Sources, *Isotop. Radiat. Technol.*, 4(2): 172-182 (Winter 1966–1967).
3. Martin Company, Nuclear Division, Strontium-90 Power Project, Final Summary Report, USAEC Report MND-SR-1676, 1960.
4. C. L. Ottinger, Oak Ridge National Laboratory, private communication, 1967.
5. P. Zahn, Development of a Radioisotope Thermoelectric Power Generator, in *Isotopic Power Generators,* Proceedings of an International Symposium, Harwell, Berkshire, England, 1966, pp. 435-450, European Nuclear Energy Agency, 1967.
6. E. E. Fowler, Radioisotopes and Radiation Developments in the USA—1967, *Isotop. Radiat. Technol.*, 5(3): 177-178 (Spring 1968).
7. The U. S. Radioisotope and Radiation Processing Industries—1968, *Isotop. Radiat. Technol.*, 6(3): 233-234 (Spring 1969).
8. U. S. Naval Nuclear Power Unit, Quarterly Reports for Radioisotope Power Devices of the U. S. Navy, Vol. 1, Nos. 1–4, 1967; Vol. 2, Nos. 1–4, 1968; Vol. 3, No. 4, 1969; and Vol. 4, Nos. 1 and 3, 1970.
9. R. E. Tomlinson, B. F. Judson, and L. L. Zahn, Large-Scale Fission Product Recovery, in *Proceedings of the Third International Conference on the Peaceful Uses of Atomic Energy, Geneva,* Vol. 10, pp. 544-550, United Nations, New York, 1965.
10. Hanford Atomic Products Operation, Hot Semiworks Strontium-90 Recovery Program, USAEC Report HW-72666, General Electric Company, Hanford Atomic Products Operation, 1963.
11. S. J. Rimshaw and E. E. Ketchen, Strontium-90 Data Sheets, USAEC Report ORNL-4358, Oak Ridge National Laboratory, 1969.
12. L. A. Bray and H. H. Van Tuyl, Laboratory Development of a Carrier-Precipitation Process for the Recovery of Strontium from Purex Wastes, USAEC Report HW-69534, General Electric Company, Hanford Atomic Products Operation, 1961.
13. R. E. Burns, R. L. Moore, A. M. Platt, and W. H. Swift, Recovery and Purification of Megacurie Quantities of Strontium-90, *Chem. Eng. Prog., Symp. Ser.*, 60(47): 1-8 (1964).
14. G. L. Richardson, Recovery of Strontium from Purex Waste by Lead Sulfate Carrier Precipitation—Pilot Plant Studies, USAEC Report BNWL-4, Battelle–Northwest, 1965.
15. R. P. Wischow and D. E. Horner, Recovery of Strontium and Rare Earths from Purex Wastes by Solvent Extraction, USAEC Report ORNL-3204, Oak Ridge National Laboratory, 1962.
16. D. E. Horner, K. B. Brown, D. J. Crouse, and B. Weaver, Recovery of Fission Products from Waste Solutions by Solvent Extraction, USAEC Report ORNL-3518, Oak Ridge National Laboratory, 1963; also, *Nucl. Sci. Eng.*, 17(2): 234-246 (1963).
17. W. Schulz, J. E. Mendel, and G. L. Richardson, Solvent Extraction Recovery and Purification of Strontium-90, USAEC Report HW-SA-2396, General Electric Company, Hanford Atomic Products Operation, 1961; also, *Ind. Eng. Chem., Process Design Develop.*, 2: 134-140 (1963).
18. G. L. Richardson, Solvent Extraction of Strontium, Cerium, and Rare Earths with D2EHPA. Part 2. Pilot Plant Studies, USAEC Report HW-79762 Pt. 2, General Electric Company, Hanford Atomic Products Operation, 1964.
19. D. E. Horner, Review of Process Technology for Recovery and Purification of Fission Product Strontium-90 (in preparation), and D. E. Larsen, Atlantic Richfield Hanford, Richland, Wash., private communication, 1970.
20. Battelle Memorial Institute, Pacific Northwest Laboratory, Division of Isotopes Development Programs Quarterly Report for February–April 1970, USAEC Report BNWL-1308-2.
21. E. Lamb, H. E. Seagren, and E. E. Beauchamp, Fission Product Pilot Plant and Other Developments in the Radioisotope Program at the Oak Ridge National Laboratory, in *Proceedings of the Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958,* Vol. 20, pp. 38-43, United Nations, New York, 1958.
22. C. W. Smith, Strontium-90 Shipping Cask Design Criteria and Hazards Evaluation, USAEC Report HW-68081, General Electric Company, Hanford Atomic Products Operation, 1961.
23. W. R. Kendall and D. W. McLenegan, Strontium-90 Shipping Cask and Protective Buffer, USAEC Report HW-68274, General Electric Company, Hanford Atomic Products Operation, 1961.
24. J. Cochran and G. Pierson, Quehanna Pilot Plant First Generation Process Operations, USAEC Report MND-3062-22, Martin Company, Nuclear Division, 1965.
25. J. C. Posey, Calorimetry for Measuring Radioactivity, *Isotop. Radiat. Technol.*, 1(1): 92-96 (Fall 1963).
26. J. C. Posey, T. A. Butler, and P. S. Baker, Hot-Cell Calorimetry for Routine Determination of Thermal Power Generated by Kilocurie Sources, in *Proceedings of the Tenth Conference on Hot Laboratories, Washington, D. C., November 26–28, 1962,* pp. 263-268, American Nuclear Society, Chicago, 1962.
27. W. D. Box and J. C. Posey, Recent Advances in Radioisotope Assay Calorimeters, *Trans. Amer. Nucl. Soc.*, 10(1): 51-52 (June 1967).
28. H. Kubota and R. F. Apple, Dissolution of Irradiated High-Fired Refractory Nuclear Materials, in *Proceedings of the Sixth Conference on Analytical Chemistry in Nuclear Reactor Technology, Gatlinburg, Tenn., 1962,* pp. 473-480, USAEC Report TID-7655, 1963.
29. ORNL Master Analytical Manual, USAEC Report TID-7015 with nine supplements, Oak Ridge National Laboratory (1953–1966).
    a. E. I. Wyatt, Gross Beta, No. 9-0733001 (Rev. 9-20-56).
    b. J. E. Morton, Strontium-89 and Strontium-90 in Aqueous Solution. Di 2(ethylhexyl)phosphoric acid–Amsco Extraction Method, No. 9-0733804, (Rev. 4-14-64), Suppl. 7.
    c. C. A. Pritchard, Other Alkali Metals in Cesium Compounds, Flame Spectrophotometric Standard Addition Method, No. 1-230009 (Rev. 8-15-61), Suppl. 4.

XUM

d. E. J. Spitzer and J. R. Sites, General Operating Conditions for Isotopic Mass Spectrometry of the Elements, No. 4-0001 (2-20-64), Suppl. 7.

e. E. J. Spitzer and J. R. Sites, Strontium, Isotopic Mass Spectrometry, No. 4-0180 (2-20-64), Suppl. 7.

30. *Book of ASTM Standards*, various parts, American Society for Testing and Materials, Philadelphia, Pa.
   a. Measurement of Beta Particle Radioactivity of Industrial Water and Industrial Waste Water, ASTM Designation D-1890, Part 23.
   b. Analysis of Radioisotopes, ASTM Designation E-181-62 (Reapproved 1967), Part 30, pp. 481-491, 1968.
   c. Sampling and Sample Preparation Techniques in Spectrochemical Analysis, ASTM Designation E-311-67, Part 30, pp. 1043-1046, 1968.
31. W. B. Mann and H. H. Seliger, *Preparation, Maintenance, and Application of Standards of Radioactivity*, National Bureau of Standards, Circular 594, Superintendent of Documents, U. S. Government Printing Office, Washington, D. C., 1958.
32. G. D. O'Kelley, Detection and Measurement of Nuclear Radiation, pp. 16-40, National Academy of Science–National Research Council, Report NAS-NS-3105, Washington, D. C., 1962.
33. R. L. Heath, Scintillation Spectrometry, Gamma-Ray Spectrum Catalog, USAEC Report IDO-16880-1, Phillips Petroleum Company, Atomic Energy Division, 1964.
34. J. A. Dean, *Flame Photometry*, McGraw-Hill Book Company, Inc., New York, 1960.
35. C. E. Harvey, *Semiquantitative Spectrochemistry*, Applied Research Laboratories, Glendale, Calif., 1964.
36. J. K. MacKenzie and R. Shuttleworth, A Phenomenological Theory of Sintering, *Proc. Phys. Soc. (London)*, **62B**: 833-852 (1949).
37. P. W. Clark, J. H. Cannon, and J. White, Further Investigations on the Sintering of Oxides, *Trans. Brit. Ceram. Soc.*, **52**(1): 1-49 (1953).
38. E. B. Allison and P. Murray, A Fundamental Investigation of Sintering Phenomena, British Report AERE-M/R-1099, 1953.
39. C. Berglund, V. L. Hammond, and B. M. Johnson, The Densification and Encapsulation of Isotopic Fuels by High Energy Pneumatic Impaction—Final Report, USAEC Report BNWL-381, Battelle–Northwest, 1967.
40. T. C. Quinby, E. E. Pierce, and R. E. McHenry, Hot Presses for Glove Box and Manipulator Cell Use, USAEC Report ORNL-TM-1900, Oak Ridge National Laboratory, 1967; also, T. C. Quinby and R. E. McHenry, A Hot Press for Radioisotope Source Development, *Nucl. Appl.*, **2**: 390-393 (October 1966).
41. J. B. Moser, R. N. Blumenthal, and D. H. Whitmore, Thermodynamic Study on Nonstoichiometric Rutile (TiO_{2-x}), *J. Amer. Ceram. Soc.*, **48**(7): 384 (1965).
42. R. G. Donnelly, Oak Ridge National Laboratory, private communication, 1967.
43. C. R. King, Vacuum Leak Testing of Radioactive Source Capsules, USAEC Report ORNL-3664, Oak Ridge National Laboratory, 1965.
44. W. K. Nichols, Jr., and W. A. McDonald, Strontium 90-Fueled Thermoelectric Generator Power Source for Five-Watt U. S. Coast Guard Light Buoy, Addendum I to MND-P-2720, USAEC Report MND-3043-1, Martin Company, Nuclear Division, 1964.

XUM

Section
II
Isotopes and Radiation Technology

Isotope Technology Development

Flow Measurements with Radioisotopes

By Robert H. Lafferty, Jr.

Supplementary Keywords: *tracer; ionization of gas; industry; industry, electric; hydrology; isotope dilution; activation analysis; activable tracer; instrument; comparison; apparatus; bibliography; hydrogen-3; sodium-24; chromium-51; cobalt-60; bromine-82; krypton-85; iodine-131; iodine-132; xenon-133; gold-198.*

Abstract. *Methods of measuring flow with radioisotopes are reviewed. Various nonradioactive flowmeters are reviewed in an introductory section to put the methods using isotopes in the proper perspective. The advantages, disadvantages, and relative costs of various methods are compared. Radioisotopes may be used to measure flows of liquids or gases in a variety of ways: as tracers; to ionize a gas and then measure the flow rate of the ions; or with various mechanical flowmeters to indicate the movement of the flowing material. The precision and accuracy of flow measurements using radioisotope tracers are also discussed.*

Author's Note: In *Isotopes and Radiation Technology*, 4(2): 93-108 (Winter 1966–1967), is an excellent review article by C. G. Clayton on the measurement of flows of liquids and gases using radioisotopes. The author of the present article acknowledges that he received considerable help from Clayton's article and other publications by Clayton and his associates at the United Kingdom Atomic Energy Authority.

The measurement of the flow of liquids, gases, and solids is a very important factor in industry, commerce, and our everyday life. These measurements range from relatively simple small-scale measurements, such as the flow of water to our homes or the flow of gasoline into our automobile, to the measurement of the flow of petroleum in a 36-in.-diameter 1500-mile-long pipeline. Obviously most of these measurements are made with permanently installed indicating or recording meters.

Measurement of flow with radioisotopes will probably never be competitive with conventional flowmeters in most routine applications. However, under the following situations, a radioisotope technique for measuring flow is the preferred method:

1. When precise flow rates are needed.
2. When an occasional measurement of the flow in a pipe is needed and no permanent flowmeter is available (i.e., for research on a process).
3. When calibration of a permanent conventional meter is required since radioisotopic tracer methods have been shown to have high accuracy and precision (see later section titled "Accuracy and Precision").

This article describes radioisotope methods for measuring the flow of liquids and gases. It covers both closed conduits and open streams. The majority of radioisotope methods for flow measurement use the isotope as a tracer, but a few nontracer techniques, such as gas ionization or use of the isotope in a mechanical device, are also discussed. The use of isotopes to follow the movement of sand in rivers and harbors and of groundwater is not included. These subjects have been covered thoroughly in several conferences (see, for example, Refs. 1 and 2). Although flow measurements are frequently made in ventilation and leak-detection studies, such studies will not be discussed here since they also have been adequately reviewed elsewhere.[3,4]

SURVEY OF FLOW-MEASUREMENT TECHNIQUES

The radioisotope technique is only one of a large number of existing techniques for measuring flow. Most of the other techniques have been discussed in

XUM

detail in standard works on measurement systems,[5,6] but the main methods are summarized here to put tracer and isotopic methods into the proper perspective.

Techniques of measurements are separated into five main types to simplify this discussion: (1) using meters that measure the velocity of the fluid directly; (2) using meters that measure the fluid flow by noting the pressure drop when flow is constricted; (3) using meters that measure the flow by observing the area required for a given flow to take place; (4) using meters that are suitable only for open streams; and (5) using tracer methods.

Direct Measurement of Velocity

The most direct way to measure fluid flow is to use the moving liquid to actuate some type of measuring device. The simplest of these devices is a vane that hangs by a pivot from the top of a pipe and is immersed in the flowing liquid. The greater the fluid flow, the greater the displacement of the vane from the perpendicular by the force of the flowing liquid. However, because of the obstruction the vane offers the stream, there will be an appreciable pressure drop across the meter.

The pressure drop of the fixed-vane meter can be overcome if a number of vanes on a wheel are substituted so that the flow causes the vane paddle wheel to rotate. With a device such as this, there is very little pressure drop involved, and translating the motion of the wheel into flow rate is a simpler mechanical problem than measuring the movement of a fixed vane.

For large flow rates where a flat-vane wheel is not suitable, the flat vanes are replaced by helical vanes or a turbine rotor with their axes parallel to the direction of flow. With such meters the pressure drop is low, and very large flows can be measured.

For the turbine-type rotor, the flow rate is frequently determined by placing a magnet in the rotor and measuring the frequency of the alternating current generated in an external coil. The magnetic flowmeter is a rather special type of velocity flowmeter which requires that the liquid whose flow is being measured be a conductor of electricity. This meter uses the principle that the flowing liquid cuts the lines of force of an electromagnet, thus generating an electric current; the electric current so generated is proportional to the flow rate. Such a meter will not measure very low flow rates. Faraday unsuccessfully attempted to use this principle with the Earth's magnetic field to measure the flow of the River Thames in London.

Pressure-Differential Methods

Probably the most common flowmeters are those in which some type of constriction is placed in the line through which the liquid is flowing and the resulting pressure drop is measured. The flow rate can be determined from the pressure drop by a suitable calibration. The flow may be constricted by an orifice plate, a Pitot-static tube,* a Venturi tube, or a flow nozzle.

The oldest and most common form of pressure-differential device is the orifice-plate flowmeter. It has been estimated that 85% of all meters installed are of this type. Even the Romans of Caesar's time used this device for controlling the amount of water delivered into the various channels of the water-supply system and to householders. Because of its simple form, the orifice plate is easy to manufacture accurately, and therefore it is cheaper in comparison with other devices involving pressure differentials. Its chief drawback is that it causes a higher pressure drop in the flowing liquid than any of the other devices, and it cannot be used when the pressure head causing the flow is already low.

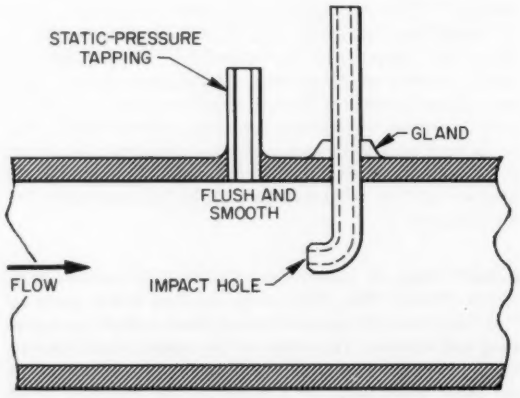


Fig. 1 Single-hole Pitot tube.

The Pitot-static tube flowmeter is an L-shaped tube that is inserted into the fluid flow with its open end facing into the stream of the fluid (Fig. 1). The fluid impinging on the tube causes an increase in pressure in the Pitot tube that can be compared with the average pressure of the stream; from the pressure difference,

*While the Pitot-static tube is not strictly a constrictional type flowmeter, it does indicate flow by measurement of a pressure differential.

the flow can be deduced. The Pitot tube actually measures the velocity of the fluid at a point, but, by traversing the stream with the tube and measuring the velocity at several points, one can obtain the average velocity. From this and the cross-sectional area, the flow can be derived. The Pitot tube causes essentially no pressure drop in the flowing fluid but can only be used at fairly high flow velocities. It is usually used as a temporary device to determine the range of flows of a system prior to installation of a permanent metering system.

The Venturi tube (Fig. 2) consists of five parts: an inlet ring of the same diameter as the upstream pipe,

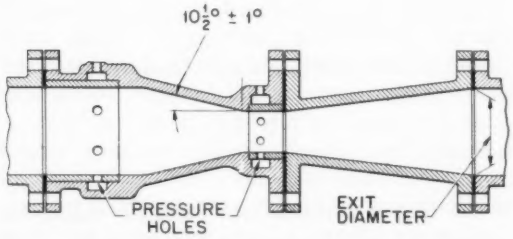


Fig. 2 Venturi tube.

with a side hole for measuring the static pressure; an entrance cone, which includes an angle of 21°, joined to the inlet by a smooth curve; a short cylindrical throat fitted with a single hole to measure throat pressure and joined to the entrance cone by a smooth curve; an exit cone that includes an angle of 10 to 30°; and an outlet flange. The pressure drop with the Venturi tube is much lower than that with orifice plates or nozzles; however, because of the length of the tube, it cannot always be installed in existing lines. It is the most expensive of all the pressure-differential devices.

The flow nozzle is essentially a very short Venturi tube having a bell-shaped entrance cone and no exit cone. It is cheaper than a Venturi tube and can be installed in an existing line with very little trouble. Since the nozzle has no exit cone, it causes a high pressure drop, although not as high as that from an orifice plate.

Variable-Area Meters

The most familiar form of a variable-area flowmeter is the rotameter. In this type of flowmeter, a float or bob is suspended in the flowing liquid, and the flow is through a tapered tube with the wider opening at the top. As the fluid flow increases, the position of the bob rises since this will increase the area of the annular space open to flow. Rotameters are available for measuring a wide variety of flows of both liquids and gases.

A modification of this type of flowmeter is the orifice-and-plug meter in which the gas flows through an orifice that has a tapered plug seated in it. In this case also, the higher the flow rate, the higher the plug will rise, thus opening a larger annular space to the flow.

Open-Channel Flowmeters

The two most widely used meters for measuring open-channel flow are the weir and the Venturi flume.

The weir is one of the oldest flowmeters known to man. It consists of a dam built across an open channel. The depth of the water flowing over the top of the dam is a measure of the flow rate. Weirs are usually classified by the shape of the channel through which the liquid flows and are usually rectangular or triangular.

The plan of a Venturi flume (Fig. 3) is similar to that of a Venturi tube with the top open. The flume has a gradual contraction to the narrowest or throat section and then a gradual expansion to the full width of the channel. As with the Venturi tube, the downstream expansion allows for head recovery. A flume can be constructed in a channel with any cross-sectional form, and various types of contractions can be used to suit individual practical conditions.

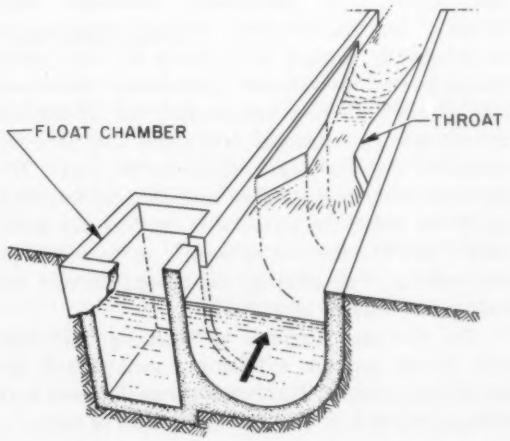


Fig. 3 Semicircular-type Venturi flume.

XUM

By careful design of the flume, the actual instrument required to indicate the flow may be simplified. If the channel is designed in such a way that the depth in the exit channel at all rates of flow is less than a certain percentage of the depth in the entrance channel, the flume will function as a free-discharge outlet. Under these conditions the upstream depth is independent of the downstream conditions, and the depth of water in the throat will maintain itself at a certain critical value at which the energy of the water is at the minimum whatever the rate of flow. When this is so, the quantity of water flowing through the channel is a function of the upstream depth only.

Tracer Methods

Probably the first person to use a tracer method to determine flow was the caveman who threw a stick in the river to see if the river was flowing too fast for him to wade across. Since this time, man has put many different substances in channel flows to find out how fast they are moving.

A good flow tracer

1. Should not be present in either high or variable concentration in the stream.
2. Must be stable to dissolved substances or gases, to suspended solids, to light, and to materials forming the stream banks and bed.
3. Must have low toxicity.
4. Should be capable of accurate determination at low concentration.
5. Should have high solubility.

Among the materials that have been used as tracers to measure flow are soluble salts of sodium, potassium, and lithium; dyes, particularly fluorescent ones; bacteria;[7] and radioisotopes. Although radioisotopes are frequently thought of as being the only useful tracers for flow measurement, this is not so. In a recent bibliography[8] on flow measurement by salt-dilution and salt-velocity techniques, only about 70 of over 200 references involved radioisotopes as the tracer. The salt-dilution method for flow measurement was originated[9] in 1863; the salt-velocity method was developed[10] in 1922; the first proposal[11] to use an isotope was made in 1922, although the isotopic method was not actually tested[12] until 1943.

The two basic methods of measuring fluid flow with tracers are the salt-dilution method and the salt-velocity method. These methods are discussed next without reference to the tracers that might be used.

Salt-Dilution Method. Fluid flow can be determined by either of two basic techniques in the salt-dilution method. One is by injection at a constant rate, q, of a soluble-tracer solution of concentration C_1 into the stream. Downstream at a point where the tracer has been completely mixed, the concentration, C_2, of the tracer in the stream is determined. The rate at which the tracer is injected is equal to the rate at which it passes the sampling point:

$$qC_1 + QC_0 = (Q + q)C_2 \tag{1}$$

where C_0 is the natural concentration of the tracer in the stream and Q is the stream flow rate. Thus

$$Q = \frac{C_1 - C_2}{C_2 - C_0} q \tag{2}$$

Usually $C_1 \gg C_2$ and $C_2 \gg C_0$, so Eq. 2 reduces to

$$Q = q \frac{C_1}{C_2} \tag{3}$$

If the flow is turbulent and complete mixing has resulted, the constant-rate-injection technique is completely independent of conduit dimensions or any variation in these dimensions. Since only the concentration of the tracer at the sampling point is needed, the sample can be taken from a branch pipe.

The other technique for determining flow is by suddenly injecting a volume, V, of tracer into the stream as a cloud. Then downstream at a point where the tracer is completely mixed, a time–concentration curve is obtained for the entire cloud as it passes. The flow can then be calculated from the relation

$$Q = \frac{VC_1}{\int_0^\infty (C_2 - C_0)dt} \tag{4}$$

where C_1, C_2, and C_0 have the same meanings as in Eqs. 1 to 3. The integral represents the total area under the time–concentration curve with the background subtracted and can be obtained from a graphical integration of a continuous record of time vs. concentration.

The advantages of sudden injection over constant-rate-injection technique (or method) are:

1. It is more economical of equipment since no apparatus for continuous tracer injection is required.
2. It is less sensitive to sampling position, provided that adequate mixing is obtained, since the requirement of operating in a region of constant concentration no longer applies.

3. Because samples removed during the transit period are mixed and analyzed as a single composite sample, only one measurement is required.

4. Operation of the constant-rate-injection technique depends critically on removal of samples during the period of constant concentration. No such restriction applies to the sudden-injection technique; only an approximate knowledge of the tracer distribution is required.

Salt-Velocity Method. The basic principle of the salt-velocity method, sometimes referred to as "peak-to-peak timing," is simpler than that of any of the other tracer methods. A cloud of the tracer is suddenly injected into the flow, and then the time for the cloud to pass between two detectors downstream is measured. Allen,[10] in proposing the method, originally detected the passage of a salt cloud in the pipe at two locations by measuring the electrical conductivity of the solution. The main advantage is that, ordinarily, simpler detection equipment can be used than that required for the salt-dilution method; however, its principal disadvantage is that it depends on an accurate knowledge of the cross-sectional area of the conduit.

RADIOACTIVE-TRACER MEASUREMENTS

The use of chemicals to trace stream flow is a technique that is well over 100 years old. One of the major drawbacks of this method is the extremely large amount of chemical that must be added to a stream so that it can be detected by chemical or physical methods. Because of this objection, Joly,[11] in 1922, suggested that a radioactive solution could be detected at much lower concentrations than other chemicals and its use should be considered in the salt-dilution methods. Joly calculated that 300 g of pitchblende dissolved in nitric acid would provide sufficient radium to be detected in an average stream. He never tried his suggested method. In 1943 Hess[12] tried the method with radium and found that it worked, although he found that he had to use more radium than Joly had calculated.

The first artificial radioisotope was used in 1946 when Karrer, Cowie, and Betz[13] used ^{24}Na, prepared in a cyclotron, with the salt-dilution method to measure condenser water flow in a power plant.

The special advantages of radioisotopes as tracers for the measurement of flow rate are

1. High sensitivity of detection. Very small amounts can be detected in situ and can be accurately measured in the field or laboratory.

2. Accurate measurement. Measurements are equally accurate in clear, turbid, polluted, or saline water—provided that elementary precautions are taken against losses by adsorption.

3. Low background levels. The natural radioactivity of water is negligible for flow measurements involving gamma-active tracers.

4. Easy measurement. Measurements can be made on existing equipment with a minimum of modification. Frequently the measurement can be made from outside the conduit or pipe.

5. Low pressure drop. Since injection devices and measurement equipment are simple, essentially no pressure drop is induced in the flowing liquid.

The disadvantages of using radioisotope tracers include

1. Radiological safety. This would probably be analogous to toxic problems encountered with chemical tracers.

2. Handling problems associated with gamma-active isotopes. These become serious only when making flow measurements at rates above 1000 ft^3/sec.

3. Licensing. In the United States a license to use isotopes must be obtained from the USAEC or from an agreement state.

4. Necessity for discontinuous measurements. This is true of all salt-dilution and salt-velocity methods.

Radioisotopes can be used as tracers with any of the techniques mentioned in the previous section—constant-rate injection, sudden injection, or peak-to-peak timing. In the total-count[14] or total-sample method,[15] to be discussed next, only radioisotopes are especially convenient as tracers.

Total-Count Method

Sudden injection of the tracer is used in this method,* but, instead of the tracer concentration being measured by evaluation of the integral $\int_0^\infty (C_2 - C_0)\,dt$ (see Eq. 4), only the total count is measured and this is done by a detector downstream from the injection point. The detector can be in the stream in the case of an open channel or on the edge in the case of a pipe. For any given amount of tracer, A, the number of counts recorded is inversely proportional to the flow rate, expressed mathematically as

$$Q = AF/N \qquad (5)$$

*The total-count method has been patented by the Chevron Research Company.[16]

XUM

where Q is the flow rate, N is the number of counts recorded, and F is a proportionality constant characteristic of the isotope, the counter, and the geometrical relationship between the counter and the stream.

In practice, F is determined from the number of counts obtained on the counter from a known concentration of tracer under the same geometric conditions that existed during flow measurements. Since reproducing the geometry of the counter and stream is difficult in open streams, often it is more convenient to pump a sample into a bucket in which the counter is placed and then return the sample to the stream.

The total-count method has several advantages over other flow-measuring methods:

1. No equipment need be installed inside the piping or the flow system.
2. Much less isotope is needed for a measurement than in the salt-dilution method.
3. The specific activity of the tracer solution does not have to be known, only the total activity.
4. The tracer may be added in a very irregular manner, in contrast to the dilution method.
5. An instantaneous reading is obtained, and, if the calibration factor, F, is known, the system can be arranged to measure flow rate directly.

The principal disadvantage is that the counting time is limited to the time required for the tracer to pass the detector, which also limits the statistical accuracy with which N can be determined.

Résumé of Radioisotope Tracer Methods

Clayton[17] classified radioisotope tracer methods as follows:

Constant-Rate Injection. This is the same as the salt-dilution method in which a radioisotope is continuously injected into the flowing stream, and then further downstream the concentration of the isotope is determined.

Sudden Injection. The isotope is introduced rapidly into the flow as a cloud, and then the wave is determined at a point downstream. There are four different ways to measure the wave:

Continuous Sample. Samples are withdrawn at regular intervals and counted. The counts for each sample are plotted against time, and the concentration is determined by measuring the area under the curve.

Total Sample. A single sample is withdrawn over a period long enough to cover the passage of the tracer, and then the average concentration is determined by taking a sample from the large sample.

Total Count. A counter is placed in the flow or on the edge of the stream, and the flow is determined by the total counts registered on the counter.

Isotope Velocity. This is the radioisotope equivalent of the salt-velocity method in which the flow is determined by measuring the time it takes the pulse to move between two counters. Use of this method requires a knowledge of the cross-sectional area of the conduit.

Table 1 is Clayton's[18] summary of the characteristics of the main methods of measuring flows.

ACCURACY AND PRECISION

In the introduction it was mentioned that radioisotope tracer methods should be used when precise flow rates are needed or when a method is needed to calibrate another flowmeter. This implies that radioisotope tracer methods are both precise and accurate. Clayton and coworkers have tested this assumption under a number of conditions and have found that it is true.

Closed Conduits

The first test made by Clayton[19] and his coworkers was on the isotope-dilution method. For this test they used a recirculating system at the National Engineering Laboratory, East Kilbride, Glasgow. This system has a 700-ft-long 20-in.-diameter pipeline in which the flow can be varied from 1 to 20 ft^3/sec, and the flow can be diverted into a tank suspended from a weighbridge so that the mass flow rate can be measured with an overall accuracy of ±0.15%.

For the test ^{24}Na, the tracer, was injected into the center of the pipe at a constant rate with a special pump, which is described in a later section. Samples were taken at the pipe axis and collected in 2.5-liter polyethylene bottles at 100 ft (60 diameters), 183 ft (110 diameters), and 366 ft (220 diameters) from the point of injection. For each test, five injections were made and five samples were taken from each sampling point. Flow rates tested were between 5 and 18 ft^3/sec, and the results were compared with the values obtained by weighing. Since it was found that mixing was not adequate at the 60-diameters sampling point, sampling at this point was discontinued in the later tests. The mean error of the results with samples taken at 110 diameters was 1.50%, the standard deviation was ±1.15%, and the spread in the errors was from

Table 1 Comparison of Methods of Flow Measurement[18]

Method	Accuracy, %	Operating range	Comments
Current meters	±1 to 2	>2 ft/sec	Delicate. Requires calibration. Pipe diameter required. Continuous measurement for short time. No head loss. Proportional to velocity.
Pitot traverse	±2	>2 ft/sec	Tedious. Involves accurate traverse of pipe along a number of diameters. Diameter required.
Standard orifice plates	±1.5	No limit if pressure difference can be monitored	Inexpensive. Clean fluids required. Large loss of head. Mostly used in smaller pipes (up to ~32-in. diameter—usually less). Continuous measurement.
Calibrated orifice plates	Up to calibration standard		
Venturi flume	±1.5		Expensive. Small loss of head. Can be used for "dirty" fluids. Continuous measurement.
Gibson method	±2	Determined by application	Pipe dimension along test section required. Involves emergency closing of pipe flow. Intermittent measurement.
Chemical dilution	±2	No limit	Intermittent measurement. No loss of head. Not dependent on cross-sectional area. Sufficient pipe length required to give complete mixing of an injected tracer.
Chemical velocity	±2	No limit	Intermittent measurement. No loss of head. Depends on knowing cross-sectional area. Sufficient pipe required for mixing.
Isotope dilution	±1.5	No limit	Same as for chemical dilution but much smaller injection volume required.
Isotope velocity	< ±1	No limit	Same as for chemical velocity but smaller injection volume required.

+0.55% to −2.26%. With samples taken at 220 diameters, the mean error was 1.56%, the standard deviation was ±1.68%, and the spread was from +1.59% to −2.14%.

In a second test at the National Engineering Laboratory, Clayton[20] determined the accuracy of the isotope-velocity method using a 20-in. pipe having a 180° bend in it. This loop was also designed so that the water flow could be measured absolutely by diverting it into a tank on a weighbridge. In this test an injector (described in a later section) was used to give an instantaneous pulse of ^{24}Na into the center of the pipe. In most of the experiments, the two detectors were separated by 125 ft (75 diameters), the first detector being 190 ft (115 diameters) from the point of injection. Clayton[20] reports that at low flow rates (5 to 7 ft^3/sec) the means of three experiments were within 0.2% of the absolute flow rate and that at higher flow rates (15 to 18 ft^3/sec) the means deviated by 0.8% from the absolute flow rate.* These accuracies were achieved when the flow rate was measured by timing the peak from one detector to the other, and it did not matter whether the detectors were separated by the 180° bend or not. When experiments were made in which the flow rate was determined by measuring the time it took the peak to get from the injector to the first detector, the error rose to about 4%.

Clayton[21] made another series of tests using a 4-in.-diameter pipe loop and a weigh tank for absolute calibration. In these tests, at flow rates from 0.12 to 0.26 ft^3/sec, he found that the constant-rate-injection, total-sample, and isotope-velocity methods all showed accuracies well within ±0.5%. The accuracy of the total-count method was slightly inferior to this.

Schuster and Hansen[22,23] of the U. S. Bureau of Reclamation, in work sponsored by the USAEC Division of Isotopes Development, measured flow rates of about 300 ft^3/sec by isotopic methods in 6- to 7-ft-diameter penstocks and compared them with flow rates determined by an orifice flowmeter. These workers used ^{82}Br and the isotope-velocity, continuous-sample, isotope-dilution, and total-count methods. The percent average deviation between the isotope methods and the orifice flowmeter, as well as the standard deviation of the isotope methods, is given in Table 2. In general, the isotope methods deviated by 2% or less from the flowmeter. The injections were made at four points on the pipe's circumference, either at the wall or 8 in. from the wall, by a device described

*Clayton's tests covered flow ranges that were only 2 or 3 to 1. Practical ranges for general industrial applications may be as high as 10 to 1. The isotopic tracer method still requires evaluation at these higher ranges.

Table 2 Deviation Between Isotope Methods and Orifice Flowmeter[23]

Method:	Isotope velocity*			Continuous sample			Total count		
Mixing length, diameters	14	45	82	36.5	105.5	105.5	105.5	105.5	919
Sample location				4 points	0.54R	0.04R	0.54R	0.04R	At turbine
Number of measurements	8	17	8	7	8	8	7	7	7
Average deviation, %	1.6	2.0	2.4	2.4	1.5	1.6	2.1	3.6	1.5
Standard deviation, %	1.6	1.8	1.2	2.6	1.8	1.9	1.7	2.2	1.6

*In the velocity method the mixing length gives the distance to the first counter; the distance between the first and second counters was 22 diameters in all cases.

in a later section. Samples in the continuous-sample and isotope-dilution methods were taken either from four points on the circumference or from a single tube at 0.54 or 0.04 of the radius (R) from the pipe wall.

Open Stream

Fewer tests to determine the accuracy and precision of radioisotope methods for open-stream flow measurement have been made than have been made for pipe flow. With ^{24}Na as the tracer, Smith, Wearn, and Parsons[24] at the UKAEA Wantage Research Laboratory compared the flow measured using the continuous-sample method with that using a weir. At flows up to 6 ft^3/sec, they found that the limits of accuracy were between ±0.3% and ±0.6%.

Clayton and Smith[25] compared the isotope-dilution and continuous-sample techniques for measuring the flow rates of four streams with ^{24}Na and ^{82}Br as tracers and found that both methods were reproducible and differ systematically by 3.1%.

Hull[14,26,27] has compared flow measurements from the total-count method with those from traditional flowmeters and found that the two methods were usually within about 5% of each other.

CHOICE OF RADIOACTIVE TRACER

In an earlier section the general requirements for any tracer were reviewed: it should not be present in the stream being measured; it should be stable to other materials in the stream being measured; it should have low toxicity; it should be easy to determine accurately; and it should have high solubility. All these requirements are involved in the choice of a radioactive tracer, and the following factors must also be considered: the radioactive half-life, the type and energy of emitted radiation, the maximum permissible level in drinking water (this is a special form of toxicity), the availability, and the cost. Since radioisotope tracers are usually used in smaller concentrations than other chemical substances, the sorption of the isotope by materials in a stream can cause trouble and should be considered carefully.

The isotopes most frequently used as tracers in the measurement of liquid flow are ^{24}Na, ^{82}Br, ^{132}I, ^{131}I, ^{51}Cr, ^{198}Au, ^{3}H, and ^{60}Co. In gas-flow measurements, ^{85}Kr, ^{133}Xe, and ^{82}Br as methyl bromide are most frequently used. Tables 3 and 4 give the radioactive and radiotoxicity properties of these compounds.

The choice of the best tracer for any application will usually involve a compromise of various factors. The pros and cons of the isotopes listed above and in Tables 3 and 4 are discussed below.

^{24}Na

The 2.75-MeV gamma emitted by ^{24}Na makes it very easy to determine in the field by counting; however, when the isotope is transported or injected into a stream or pipe, considerable shielding of the injector sample is required because of the hard gamma. Clayton and coworkers used this isotope successfully in pipe-flow measurements with both the isotope-dilution[19] and isotope-velocity[20] methods. In work with stream flows over long distances, they found that ^{24}Na was sorbed over a 2- to 5-hr period if inert NaCl was not added.

^{82}Br

The short half-life and high-energy-gamma emission (1.47 MeV) of this isotope make it very useful for flow tests that can be run quickly. Schuster and Hansen[22,23] used it in most of their work with turbine penstock flows, and Clayton[25] compared it with ^{24}Na, ^{32}P, and ^{3}H in open-stream flow measurements. It can also be measured easily in the field.

XUM

Table 3 Isotopes Most Frequently Used as Tracers for Liquids[28,29]

Isotope	Half-life	Decay scheme β, MeV	Decay scheme γ, MeV	MPC,* μCi/cm³
^{24}Na	15 hr	1.39 (100%)	1.37 (100%) 2.75 (100%) 0.51 (99%)	2×10^{-3}
^{82}Br	35.4 hr	0.44 (99%) Others	0.55 (72%) 0.62 (44%) 0.78 (83%) Others up to 1.47 (7%)	3×10^{-3}
^{131}I	8.06 days	0.61 (90%) Others	0.36 (82%) Others	2×10^{-5}
^{132}I	2.3 hr	0.72 to 2.12 Others	0.52 (16%) 0.65–0.67 (112%) 0.77 (76%) Others	6×10^{-4}
^{51}Cr	27.8 days	–	0.32 (10%) X rays	0.02
^{198}Au	2.70 days	0.97 (99%)	0.41 (96%)	5×10^{-4}
^{3}H	12.3 years	0.018	–	0.03
^{60}Co	5.26 years	0.32	1.17 (100%) 1.33 (100%)	5×10^{-4}

*The MPC (maximum permissible concentration) is given for exposure for a 168-hr week.

Table 4 Isotopes Most Frequently Used as Tracers for Gases[28,29]

Isotope	Half-life	Decay scheme β, MeV	Decay scheme γ, MeV	MPC, μCi/cm³
^{85}Kr	10.7 years	0.67 (99%)	0.51 (0.42%)	3×10^{-6}
^{133}Xe	5.3 days	0.34	0.081 (36%)	3×10^{-6}
^{82}Br	See Table 3			4×10^{-7}

^{131}I

This isotope in the form of the iodide is reported as having uncertain sorption behavior at very low concentrations. However, its half-life is extremely convenient for stream-discharge measurements. It requires less shielding than ^{24}Na and ^{82}Br. It has greatest radiotoxicity.

^{132}I

For very short experiments measuring flow, ^{132}I ($T_{½}$ = 2.3 hr) has been suggested by Clayton[25] and used by Smith and Clark.[30] This isotope is conveniently obtained in the field by elution from ^{132}Te ($T_{½}$ = 78 hr) adsorbed on an alumina column. The short half-life of this isotope permits consecutive experiments without interference from previous injections.

^{51}Cr

This isotope is frequently used as the ethylenediaminetetraacetic acid (EDTA) complex, a form of the isotope suggested by Lacy and de Laguna.[31] In a double-tracer experiment testing groundwater flow, Knutsson, Ljunggren, and Forsberg[32] showed that the flows of the ^{51}Cr–EDTA complex and tritiated water (HTO) were identical. Heemstra, Watkins, and Armstrong,[33] on the other hand, showed that the ^{51}Cr–

EDTA complex was not a good tracer to use in studying the flow of brine through permeable sandstone.

^{198}Au

The 0.41-MeV gamma ray from this isotope makes it particularly suitable for flow measurements of open streams by the total-count method. Hull[27] and Timblin and Peterka[34] have used this isotope in this way. It is usually used in the form of gold chloride. Timblin and Peterka[34] reported some evidence in their experiments that the gold was sorbed on the aquatic weed in the channel where they were measuring flow rates.

Tritium (^{3}H)

Hydrogen-3 in the form of HTO should be an ideal tracer for water because it is essentially the same as water and practically is not subject to sorption. Clayton and Smith[25] compared it with ^{24}Na, ^{82}Br, and ^{32}P in open-stream flow measurements and found that it was convenient to inject in the field because of the weak beta radiation; however, the chief drawback is that it cannot be determined in the field because of the weak beta radiation and must be taken to the laboratory. Knutsson, Ljunggren, and Forsberg[32] tested HTO and ^{51}Cr–EDTA together in a double-tracer experiment on the flow of groundwater and found that the movements of the two isotopes were identical. In this case they considered the tritium as the standard that was proving that ^{51}Cr–EDTA could be used.

The most serious objection to the use of tritium in streamflow measurements is its possible interference with the dating of groundwaters by cosmic-ray-produced tritium. This objection is not too serious because generally the hydraulic connection between rivers and groundwater systems is in the opposite direction, i.e., groundwater feeds the rivers and constitutes their base flow.

^{60}Co

The 1.17- and 1.33-MeV gammas from ^{60}Co make this isotope easy to measure in the field; however, its long half-life (5.26 years) is sometimes a drawback. Halevy, Nir, Harpaz, and Mandel[35] had tested potassium hexacyanocobaltate (III) [$K_3Co(CN)_6$] and ^{60}Co–EDTA as tracers for groundwater flow and found that in the aquifers where they were working the $K_3Co(CN)_6$ was a very satisfactory tracer.

Activable Tracers

In some instances it will not be convenient or possible to use a radioisotope as a tracer in the measurement of flow rates, particularly if the stream in which the flow rate is being measured is used as a source of drinking water. In such instances it may be possible to use a stable isotope or compound and then determine by activation analysis the amount of the tracer that is present. In two articles Greene reviewed this technique. The first[36] dealt with general aspects of the technique and its use in medicine and pollution studies; the second[36] discussed its uses in hydrology.

Two papers reviewed by Greene are particularly pertinent to flow-measurement work. Gardner and Dunn[37] used sodium and manganese salts and then determined them by activation in the Oak Ridge Graphite Reactor. In the activable-tracer tests, they used the total-sample method and checked it with the total-count method, using ^{198}Au as the tracer.

The second paper on flow measurement was by Kobayashi and Nukazawa,[38] who used a double-tracer method for measuring river flow. In this study these workers used ^{24}Na as a tracer to indicate when the nonradioactive NaBr or NH_4Br was about to arrive at the sampling station; then they took continuous samples and analyzed them by neutron activation of the ^{82}Br. By using a combination of a radioactive and a nonradioactive tracer, they were able to inject very small amounts of radioactive tracer into the stream and thus limit the number of activation analyses that were required for determination of the flow rate.

^{85}Kr

This isotope is used more frequently than any other in determining flow rates of gases because of its high specific activity, ease of handling and storage, long half-life, and low toxicity. It is an almost pure beta emitter, and therefore the counter must be placed in the gas-flow stream or a sample must be removed from the stream for counting. Berry, Clayton, and Webb[39] used this isotope and the total-count method to measure the flow of gas in a high-speed gas-reaction vessel, and Fries[40] also used it with the total-count method to measure the flow of noncondensable gas in a synthetic-ammonia plant.

^{133}Xe

Although ^{133}Xe has not been used as frequently as ^{85}Kr, some workers consider it a better tracer for gas-flow measurement than ^{85}Kr. Specifically ^{133}Xe

has a shorter half-life and is a gamma emitter; so it is easily counted in the field.

Johnson[41] used this isotope with the dilution technique to determine flows in a chemical plant. In some of his tests, he determined the ^{133}Xe by direct on-line counting, and in others he concentrated the ^{133}Xe by condensing it in a liquid-nitrogen trap and then counted the trapped xenon.

^{82}Br

To take advantage of the good radiation properties of ^{82}Br, some workers have used this isotope in the form of ethyl bromide. Johnson[41] reports that he has had trouble with this material in a wet stream because of hydrolysis, and Clayton[18] chose ^{85}Kr rather than ethyl bromide because the ^{85}Kr was available at much higher specific activity.

INJECTION OF TRACER

One of the most important factors in achieving accurate flow measurements with a tracer is injection of the tracer into the flow in a way that will ensure complete mixing of the tracer with the stream. If complete mixing is not achieved, obviously the measurement of the flow rate will either be too high or too low. This requirement for complete mixing applies to both constant- and sudden-injection methods, although it is much more important in constant injection.

Discussed first in this section are the effects of various methods of tracer injection on mixing distance. That discussion is followed in order by descriptions of methods for continuously injecting tracers into liquids, instantaneously injecting tracers into liquids, and injecting tracers into gases. Most of these methods apply to injection into closed pipes and conduits since injection into open streams is usually as simple as pouring a bottle of tracer into the stream or releasing the tracer from a Mariotte flask or other simple device. For a wide stream the injection is sometimes made using a trough device so that the tracer can be injected into the full width of the stream at the same time.

Mixing Distance

Many workers have attempted to calculate the minimum distance required to achieve complete mixing of the tracer and the flowing medium in both streams and pipes. Taylor has made a very complete theoretical analysis of diffusion of tracers in both laminar[42] and turbulent[43] flow. Hull[27] has derived the formula for calculating the minimum distance required for complete mixing as

$$L_{min} = 50Q^{1/3} \quad (6)$$

where L_{min} is the minimum length in feet required for complete mixing and Q is the flow rate in cubic feet per second. For certain streamflow measurements made by Hull, this formula seemed to work. However, Clayton and Smith[25] and Timblin and Peterka[34] found that it was not very satisfactory. Most workers[44] in the field now feel that to expect to accurately predict mixing lengths to a factor of less than 2 is probably overly optimistic. The only way to be sure that proper mixing has been achieved is to take samples from several points across the stream and check to see that all analyses agree within experimental error.

Clayton, Ball, and Spackman[45] tested various methods of injection of the tracer to see which produced the fastest mixing in pipes. In these tests they worked with a 10-cm pipe and constantly injected the isotope. The injection positions chosen were (1) a single orifice at the pipe wall; (2) a single orifice on the pipe axis; (3) four orifices at 90° intervals around the pipe wall; and (4) four orifices at 0.63 of the radius from the wall of the pipe. Then ten samples were taken at different positions in the pipe, each sample was counted, and the differences in counting rates were compared. In every test, and at all flow rates, the injection at 0.63 of the pipe radius achieved the fastest mixing. The results of a typical run are shown in Fig. 4.

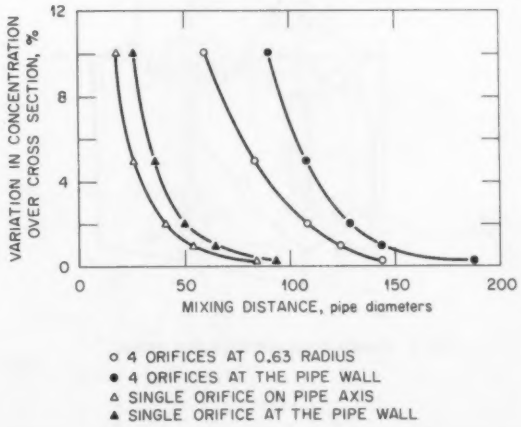


Fig. 4 The effect[47] of allowable concentration variations on mixing distance for four injection systems at a Reynolds number of 7.7×10^4.

In another experiment, Clayton[46] tested the effect of injecting the isotope into the intake of a mixed flow (part centrifugal, part axial) pump on mixing efficiency. In this test a 20-in. pipe was used, and the flow rate was 8.2 ft^3/sec. Samples taken across 2 diameters of the pipe at 90° to each other just beyond the discharge of the pump showed that even in this short distance the tracer was completely mixed. Clayton warns, however, that these results cannot be extrapolated to other pump types.

Constant-Injection Methods

For the most accurate continuous injection of tracer, a precision single-stroke displacement pump is required. Clayton[19] and coworkers described a pump they have tested extensively (Fig. 5). This pump is operated by a synchronous motor and has an accurately machined cylinder. The measured error in the injection rate of the pump was less than ±0.05%; other specifications are

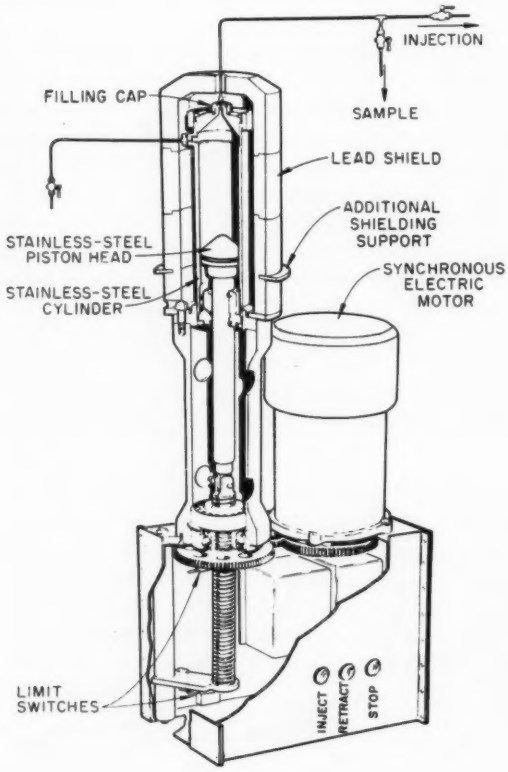


Fig. 5 Constant-velocity injection pump.[19]

Diameter	2.751 ± <0.001 in.
Volume	46 $in.^3$
Linear velocity of piston	0.804 in./min
Maximum permissible back pressure	200 $lb/in.^2$
Output	4.78 $in.^3$/min (1.30 ml/sec)

Clayton and Evans[47] described a more recent version of this pump (Fig. 6) that has a carrying handle, portable lead shielding, and a gear selector to provide three optional injection speeds.

A common practice in water-flow measurement using radioactive-tracer techniques is to inject the tracer into an intermediate pipe containing water that is continuously pumped into the conduit. This "secondary" circuit has a flow rate several times that from the injection pump and thus provides a carrier fluid for the small volume of tracer. The water in the secondary circuit can be supplied from an independent source or can be drawn from the main conduit by means of a "secondary pump" and then reintroduced into the conduit. Variations in flow rate in the secondary circuit are not important, provided that the transit time of the tracer in the secondary circuit is short compared with the transit time in the main fluid.

A secondary circuit has several advantages. Principally, the larger flow rates avoid the possibility of small orifices becoming blocked, and the increased momentum available at the point of injection into the main flow enables the tracer to be injected well away from the wall. The dilution of the tracer which occurs in the secondary circuit (~1/1000) and the increased momentum also help to reduce the mixing distance.

High-velocity jet injectors can be used with the secondary circuit to spread the tracer laterally and consequently reduce mixing distance. Two designs are illustrated[48] in Fig. 7. Each jet is arranged so that the amount of tracer injected is proportional to the flow in the entrained region at the end of the jet. Use of rectangular orifices with the long sides about 20 times the short sides and with the long sides arranged in the plane of flow can produce a large jet range. Directing the jet upstream permits impact mixing to be achieved. The design in Fig. 7*b* has the advantage of being subjected to only a small force from the fluid in the duct, but satisfactory operation is more difficult to achieve than with the design shown in Fig. 7*a* because some of the jets are directed through regions of increasing and decreasing velocity profile. When jet injectors are used, it is most convenient to inject the

XUM

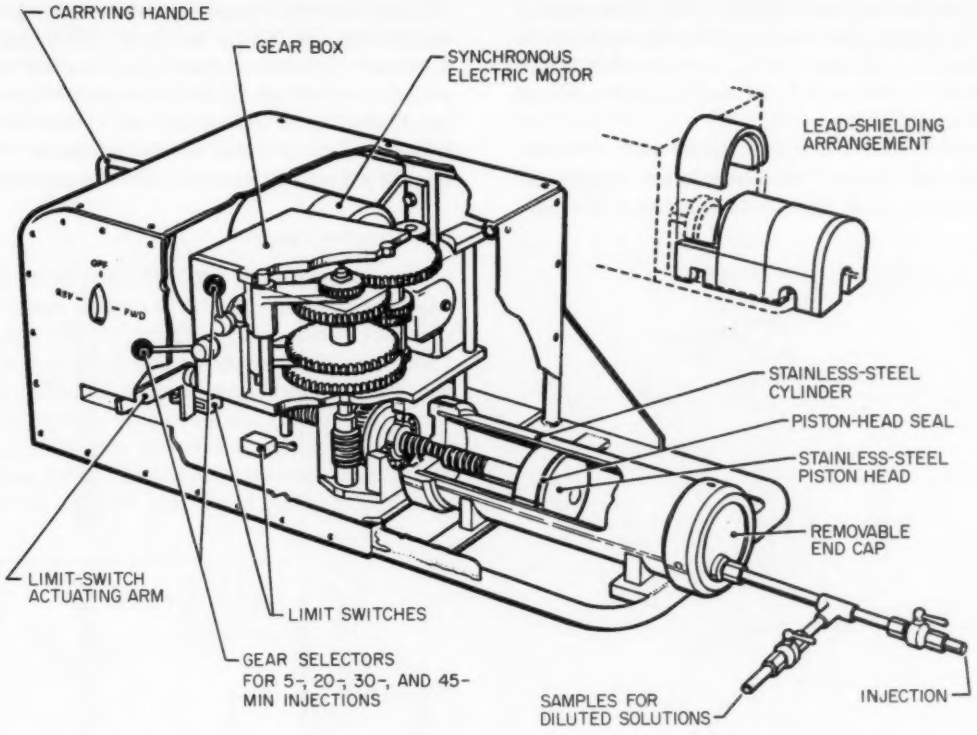


Fig. 6 Modified constant-rate injection pump.[47]

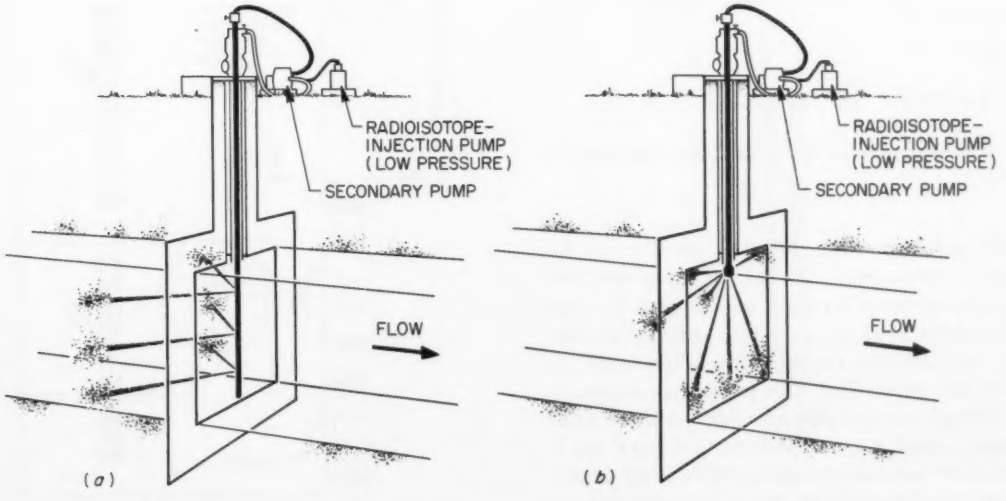


Fig. 7 Secondary pump with high-velocity jet injectors.[48] (*a*) Jets into flow stream. (*b*) Jets perpendicular to the flow stream.

tracer into the secondary circuit, which is then used to drive the jets; in this way a high momentum can be obtained. In the designs of Fig. 7, the secondary flow is obtained from the main fluid using an annular channel outside the jet probe.

Rather than inject the tracer with a motor, Schuster and Hansen[23] used compressed nitrogen and the system shown in Fig. 8 in their studies of flow rates

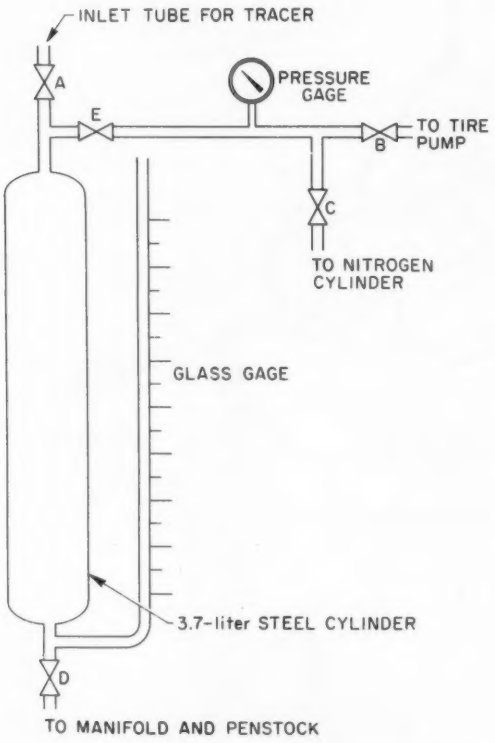


Fig. 8 Continuous-injection system using compressed nitrogen pressure.[23]

through penstocks. The penstock pressure at the injection location was ~35 psi, and they did their injection using about 70 psi nitrogen pressure. To make a measurement, they put a measured amount of tracer in the steel cylinder through valve A and filled the cylinder with water. They then pumped air with a tire pump through the sight glass and water–tracer mixture by opening valves B and A and closing valves C and E. Two to three minutes was sufficient for good mixing. The capacity of the cylinder was 3.7 liters, and it was usually filled with about 3 liters of water–tracer mixture. The cylinder was volumetrically calibrated and provided with a gage-glass scale for determining the volume injected. Timing was done with a stopwatch. To make a tracer injection, they applied nitrogen pressure through valve C and a regulator while valves A and B were closed and valves E and D were open. The solution of tracer was injected at about 5 ml/sec through a four-way manifold into the penstock flow.

Instantaneous Injection

Any of the devices described above for continuous injections of tracers may also be used for instantaneous injections lasting for very short periods—say 1 or 2 sec. Such injections are suitable for flow determination by the total-count method but may not be satisfactory for the isotope-velocity method. In addition to the devices mentioned previously, another injector used successfully in the total-count method is a modified Sparklet bottle (Fig. 9). (The unmodified

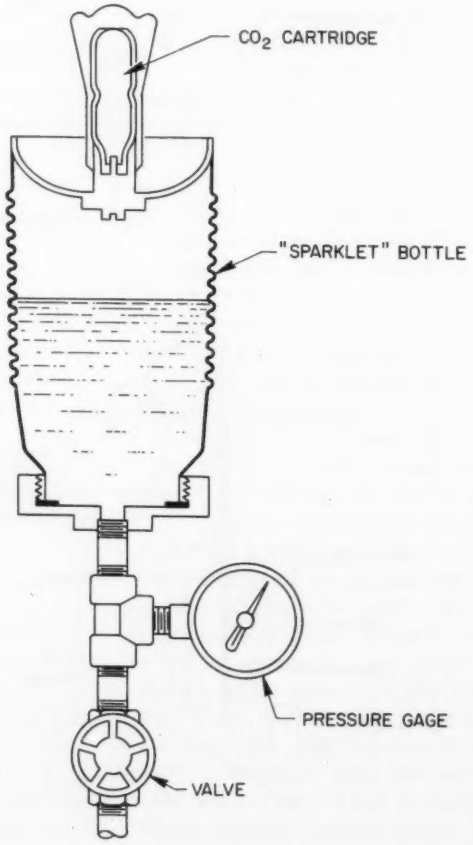


Fig. 9 Pressurized injector for liquid tracer.

bottle was designed for making carbonated water.) The bottle is modified by adding a valve and pressure gage to the outlet after filling the bottle with the tracer. After the bottle is connected to the tracer-supply line, a CO_2 cartridge is screwed down to admit the gas, and the valve is opened; when there is no further drop in the pressure gage reading, the injection is complete.

For even faster injections than those which can be obtained with the above-mentioned methods, a device described by Clayton[20] will inject the tracer solution in 15 msec (Fig. 10). The radioisotope is introduced into the side arm either as a liquid from a separate container or in a small glass ampul that can be broken by the striker. The volume injected is ~1 ml. Once the

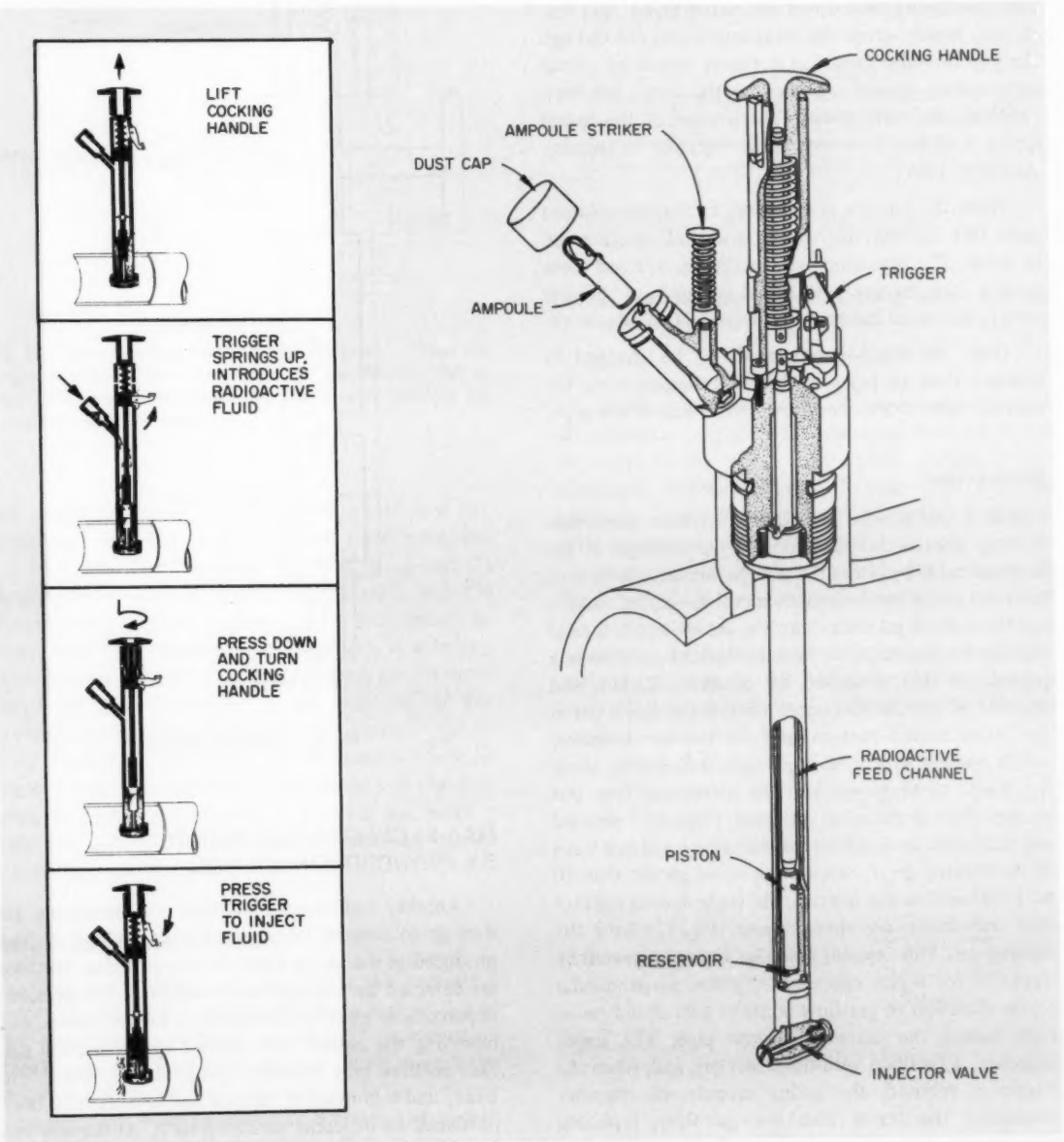


Fig. 10 High-speed injector.[20]

radioisotope has been introduced, the instrument is actuated by raising the cocking handle until the trigger engages. The cocking handle is then pushed down and the spring is compressed against the bottom of the spring compartment, which is held in position by the trigger. A bayonet socket retains the lever in this cocked position when the lever is rotated through 30°.

The trigger is pressed to eject the solution into the pipe, the spring then drives the piston down, and this, in turn, rapidly drives the volume of liquid out through the injector valve (which is normally closed by a small compression spring). As soon as the liquid has been expelled, the valve closes. The tension of the return spring is chosen to complete the injection in approximately 15 msec.

When the injector is recocked, radioactive solution again fills the reservoir so that a second injection can be made. The operating parts of the injector and those coming into contact with liquid are made of stainless steel to minimize corrosion.

Only the injector end needs to be changed to measure flow in pipes of different diameters; so the injector valve is always on the center line of the pipe.

Gas Injection

Since continuous injection of tracer gases into flowing gases is difficult, most determinations of gas flow are made by either the isotope-velocity method or the total-count method. Both methods require sudden injection of the gas tracer into the gas stream. A typical injector for gas tracer to measure natural-gas flow in a pipeline is that described by Kniebes, Burket, and Staats[49] (Fig. 11). The injector holds the tracer gas in the 50-ml central portion, and the two check valves, which operate with a 50-lb pressure differential, allow the tracer to be blown into the natural-gas flow but prevent flow in the other direction. Clayton[18] pointed out that such an injection can introduce a shock wave in the flowing gas if compression ratios greater than 10 to 1 are used in the injector. He suggested an injector that introduces no shock wave (Fig. 12) into the flowing gas. This injector is similar to one suggested by Taylor[43] for liquid injection. A piston perpendicular to the direction of gas flow contains two chambers—each having the diameter of the pipe. The upper chamber, *A*, is filled with the tracer gas, and, when the trigger is released, the spring propels the chamber containing the tracer into the gas flow, replacing chamber *B*. With this method the 3 ml of gas in the chamber is inserted into the gas flow in 2 to 3 msec.

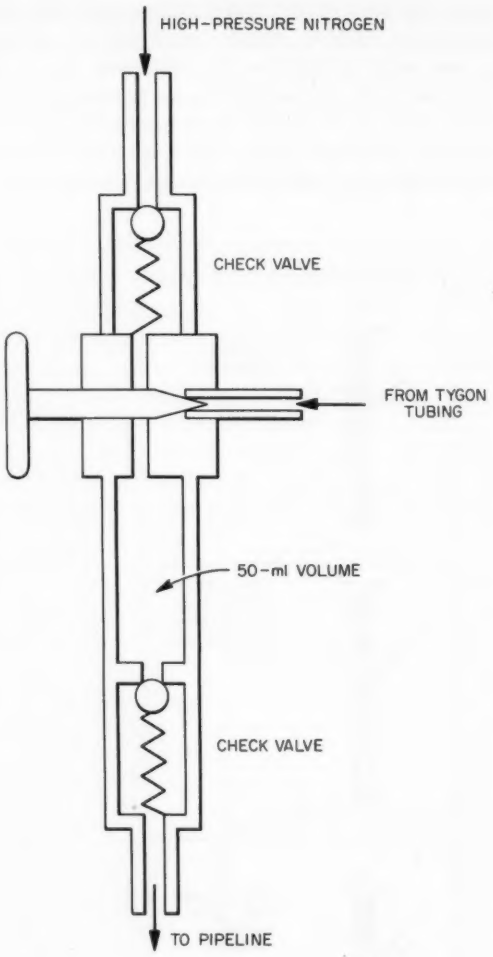


Fig. 11 Gas-tracer injector.[49]

GAS-FLOW MEASUREMENTS BY INDUCED IONIZATION

Another radioisotope method for measuring gas flow is to observe the movement of a cloud of ions produced in the gas by alpha or beta particles. The ions are detected by putting two electrodes in the gas flow, impressing an electrical potential on the electrodes, and observing the current flow caused by the ionized gas. This method was originally proposed by Blake[50] in 1928, and a number of patents and articles have been published on different variations of it. At the moment no commercial instruments based on it are available, and it is little used industrially. This lack of commer-

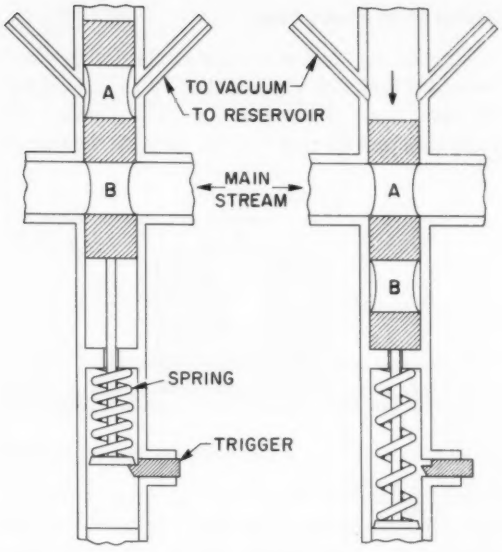


Fig. 12 High-speed injector for radioactive gases.[18] When the trigger is released, the spring drives the chamber (*A*) that is filled with a radioactive gas into the main stream, replacing the section (*B*) normally present.

cial acceptance seems odd when one considers a few advantages that this method has over tracer methods: (1) no radioactivity is added to the flowing gas; (2) measurements can be made continuously; and (3) instantaneous changes in flow can be detected. Compared with most conventional flowmeters, it induces a much smaller pressure drop in the flowing gas. Methods based on the ionization of gas may be of the continuous-ionization or the pulsed-ionization type. In 1968 Toudoire[51] published a Ph. D. thesis in which he made a rather comprehensive theoretical and practical study of both types of methods. Clayton and Webb[52] have also published a similar study of the continuous-ionization method.

Continuous-Ionization Methods

The basic design of the continuous-ionization system in which the ionization source is upstream of the detector as proposed by Blake[50] is shown in Fig. 13. At low flow rates the ions move toward the detector but recombine before arrival. As the flow rate increases, ions start to reach the detector and current starts to flow. The collector current then continues to increase as the flow rate increases. Mellen[53] received a patent on a flowmeter that had two detectors, one on each side of the source. The detectors were close enough to the source that, when there was no gas flow, there was a small current flow in each detector. This type of flowmeter obviously measures both amount and direction of flow.

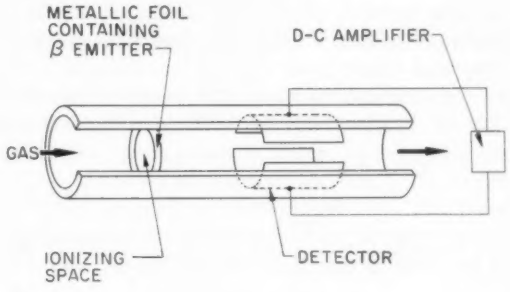


Fig. 13 Basic diagram of flow-measuring system with the ionizing source upstream of the detector.[50]

Lovelock and Wasilewska[54] described an omnidirectional anemometer that measures both speed and direction of the wind. This device consists of two concentric spherical, openwork cages with a central spherical electrode coated with ^{210}Po. It will measure wind velocities of 0 to 1000 ft/min.

Obermaier[55] described the system shown in Fig. 14 in which the source and detector are located at the same place in the gas stream. In this type of flowmeter, the faster the gas is flowing, the smaller the current indicated by the ionization chamber because more of the ions will be swept away before they can conduct a current.

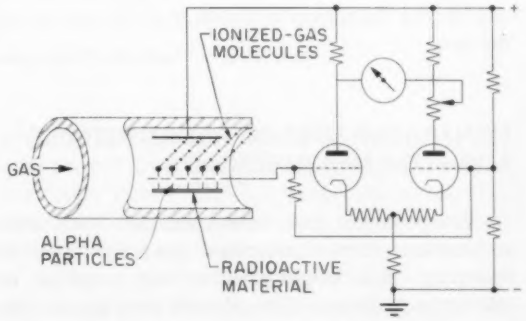


Fig. 14 Measurement of gas flow by induced-ionization system with ionizing source and detector at the same point.[55]

Pulsed-Ionization Method

The principle of this method is the same as the previously described isotope-velocity method except that, instead of measuring the time for an isotope to move between two points, it measures the flow time of a cloud of ions. With the method as originally suggested[56] a spark source was used to give the pulse of ions; however, radioisotopes are just as satisfactory and much safer if the flow of a flammable gas is to be measured.

The apparatus used in this method is shown in Fig. 15. Toudoire[51] in his work on pulsed-ionization

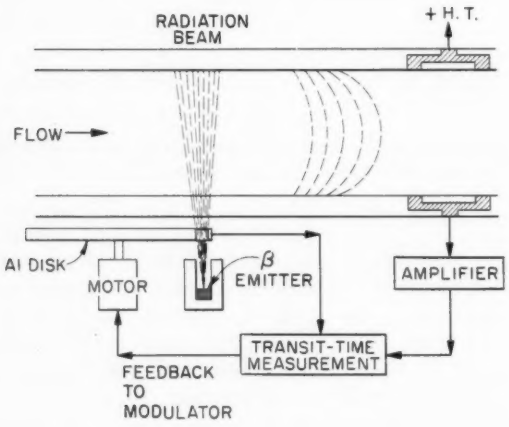


Fig. 15 Pulsed-ionization method of gas-flow measurement.[51]

methods studied mechanical modulation of the ion beam, as shown in Fig. 15, and the modulation effected by putting another pair of collector electrodes in the gas stream between the source and the collector and varying the current to discharge all the ions part of the time.

NONTRACER USES OF RADIOISOTOPES FOR FLOW MEASUREMENTS

Radioisotopes have been combined with more conventional flow-measurement methods such as deflecting strips, hinged gates, rotating propellers, or rotameters to measure flow. Most of these applications have been in systems where high temperatures and pressures or the corrosive nature of the liquid made transmission of a conventional signal difficult.

Source on an Elastic Sheet

One of the simplest of these mechanical devices for measuring radiation was described by Shumilovskii and Mel'ttser[57] and is shown in Fig. 16. The source (3) is suspended on a sheet in the fluid flow. As the flow rate

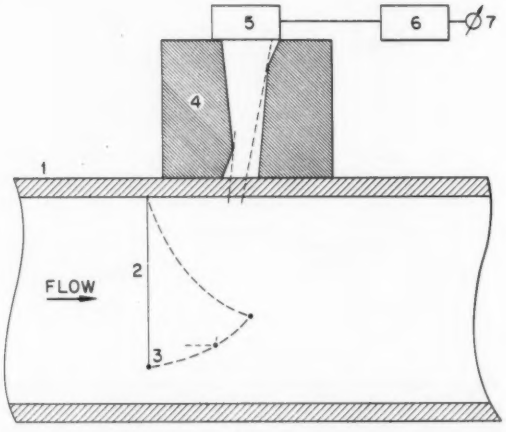


Fig. 16 Measuring the volume flow of a liquid from the position of an elastic sheet.[57]

increases, the source moves along the path indicated by the dotted curved line at the bottom until it reaches a point on the axis of the collimator (4) and the detector (5). The total flow is shown on a meter (6) and the instantaneous flow rate on a meter (7). At this point the reading of the radiation intensity will be at a maximum. Further increase in flow will result in a decrease in radiation intensity. The output meter is calibrated in terms of volume flow.

Hinged Gate with Radioactive Source

Clayton and Webb[58] established the general characteristics of a flowmeter using a hinged gate and a radioactive source (Fig. 17). The gates in these devices may be solid or may have various sized holes in them depending on the flow rate. The radiation detector used was a small cadmium sulfide crystal. If the range of flow rates to be measured varies widely, two detectors may be used as shown. At the lower end of the range, detector *B* should be used; at the upper end of the range, detector *A* would function. Clayton and Webb estimated that such a meter can be used in measuring gas flows between 1 and 1000 ft^3/hr.

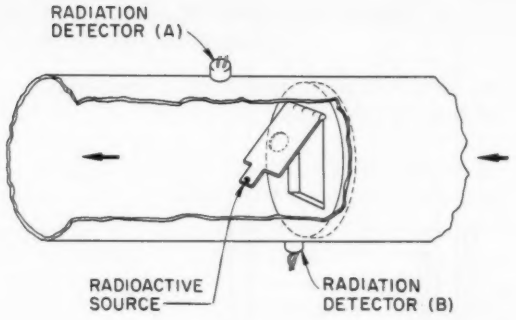


Fig. 17 Hinged-gate method of flow measurements.[58]

Rotating Propellers with Sources

Another type of mechanical flowmeter in which radioisotopes give a signal is a rotating propeller with a source embedded in one vane. Such a flowmeter has been described by Shumilovskii, Gushchin, and Tolokonnikov[59] (Fig. 18). In Fig. 18 the measuring device is a frequency meter that counts the number of pulses of radiation "seen" by the counter. These counts are recorded on meters, one of which is graduated in units of instantaneous flow rate and the other as total-volume flow. This meter was designed to operate in corrosive atmospheres or high pressures.

Carlson, Cederberg, and Ljunggren[60] used a similar propeller device to measure the flow of water in the downcomer of a boiler operating at 2000 psi and 520 to 540°C. They embedded two ^{60}Co sources, one of 10 mCi and the other of 3 mCi, displaced 120° relative to each other. By recording the pattern of radiation that appeared on the detector, they were able to determine not only the rate but also the direction of flow. An interesting part of this study was that they used an isotope-velocity method with ^{82}Br as a tracer to check the flow rate determined with the propeller.

Rotameter with Radioactive Float

Cameron, Berry, and Taylor[61] used a traditional glass rotameter enclosed in a stainless-steel tube and a float with 80 μCi of ^{60}Co embedded in it to measure low flow rates at 300°C and 2000 psi. They placed a scintillation counter at the bottom of the flowmeter, and, as the flow rate increased and the float rose, the radiation recorded by the counter fell. This meter could measure flow rates from 0 to 100 cm^3/min and, at a flow rate of 50 cm^3/min, had an error of ±1 cm^3/min.

Orifice-Plate Flowmeter with ^{60}Co in Manometer

Hencke and Cole[62] used an orifice-plate flowmeter similar to that shown in Fig. 19 to measure the flow of hydrogen in a hydrogenation system where the pressures were 5 thousand psi or higher and the temperatures were 1500°F (815°C). In this flowmeter, ^{60}Co was floated on the low-pressure side of a mercury manometer in a stainless-steel tube so that the position of the top of the mercury could be easily determined with a counter. With another modification of this meter, these workers suggest that ^{60}Co could also be put on the high-pressure leg of the manometer. In this way the difference in heights of the two legs can be

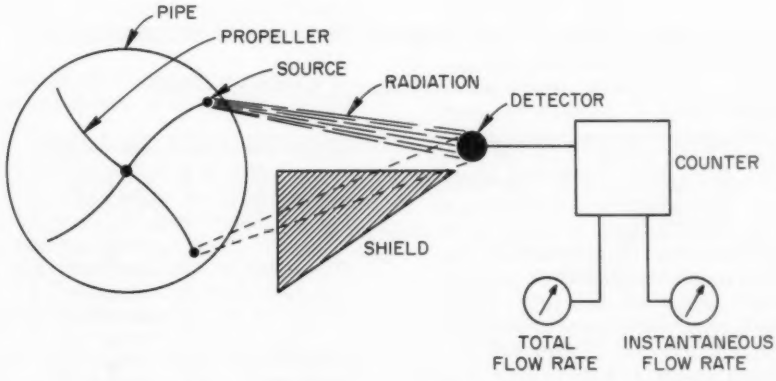


Fig. 18 Block diagram of a frequency-type flowmeter.[59]

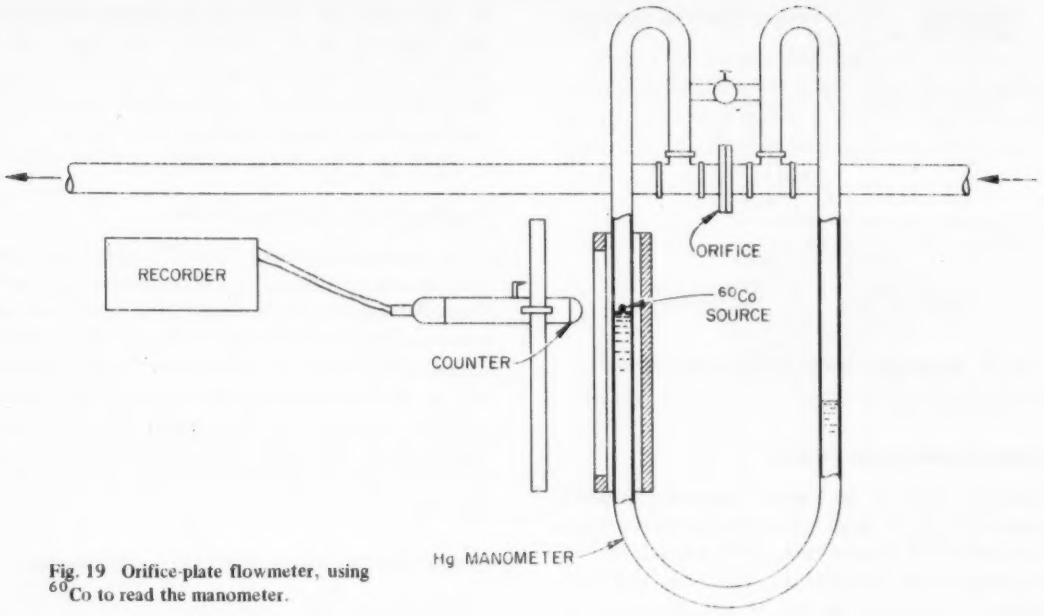


Fig. 19 Orifice-plate flowmeter, using ^{60}Co to read the manometer.

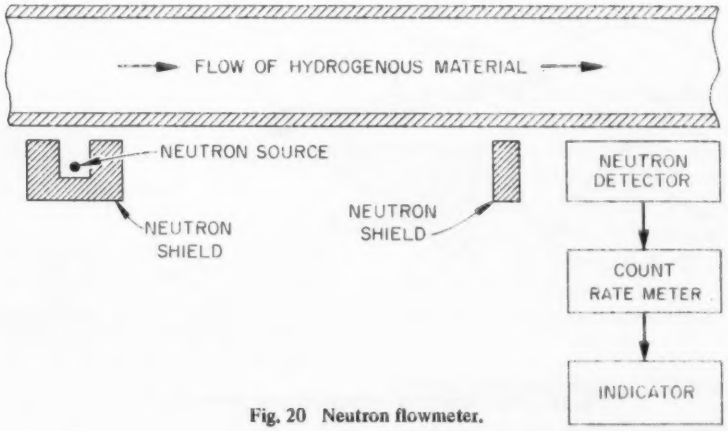


Fig. 20 Neutron flowmeter.

determined directly and variations in the temperature of the mercury will not affect the reading of the instrument. These devices allow the operator to read the manometer without actually seeing the mercury levels.

Neutron Flowmeter

Hahn[63] described a method for measuring the flow of hydrocarbons or other hydrogenous materials by irradiating the flowing material with a source of fast neutrons and then measuring the thermal neutrons at a point downstream. Such a device is shown in Fig. 20 and, of course, depends on the thermalization of the fast neutrons by the hydrogen in the hydrocarbons. For any given hydrocarbon the counting rate at the neutron detector will be proportional to the flow rate of the fluid in the pipe. This device can be used with either a constant or a pulsed neutron source.

XUM

APPLICATIONS OF RADIOISOTOPE FLOW MEASUREMENTS

Radioisotope methods have been used both routinely and for research in many industries and for hydrologic studies.

The use of isotopes to measure flow in industry has been reviewed exhaustively by Ljunggren[64] in a paper having 192 references. Some of the industries that have used radioisotopes for flow-rate measurements and are reviewed in Ljunggren's paper are petroleum refining, pulp and paper, mineral concentrates and mining, glass, sugar, and cement.

The uses of radioisotopes to measure flow in hydrologic studies have been reviewed in two IAEA conferences.[1,2] The main uses in these fields are to measure the flow of streams and canals, to measure the flow of groundwaters, and to measure the flow of sediment and sand.

REFERENCES

1. *Radioisotopes in Hydrology*, Symposium Proceedings, Tokyo, 1963, International Atomic Energy Agency, Vienna, 1963 (STI/PUB/71).
2. *Isotopes in Hydrology*, Symposium Proceedings, Vienna, 1966, International Atomic Energy Agency, Vienna, 1967 (STI/PUB/141).
3. M. Gerrard, Measurement of Ventilation Rates with Radioactive Tracers, *Isotop. Radiat. Technol.*, **5**(4): 278-280 (Summer 1968).
4. M. Gerrard, Leak Detection with Radioisotope Tracers, *Isotop. Radiat. Technol.*, **6**(1): 44-57 (Fall 1968).
5. E. B. Jones, *Instrument Technology, Vol. I, Measurement of Pressure, Level, Flow, and Temperature*, 2nd ed., pp. 107-227, Butterworths, London, 1965.
6. National Engineering Laboratory, *Flow Measurement in Closed Conduits*, 2 vols., Symposium Proceedings, East Kilbride, Scotland, 1960, Her Majesty's Stationery Office, Edinburgh, 1962.
7. A. James, Flow Measurement Using Microbiological Tracers, in *Dilution Techniques for Flow Measurement*, V. K. Collinge and J. R. Simpson (Eds.), pp. 94-98, University of Newcastle upon Tyne, Department of Civil Engineering, Bulletin No. 31, 1964.
8. R. W. Filmer and V. M. Yevdjevick, Bibliography and Discussion of Flow Measurement by Salt-Dilution and Salt-Velocity Techniques (Turbulent Diffusion of Soluble Tracers), Colorado State University, Report CER66-67RWF-VMY23, November 1966; also available as USAEC Report TID-23737.
9. M. Th. Schloesing, New Method for Gaging Fluids (in French), *Comp. Rend.*, **57**: 164-166 (1863).
10. C. M. Allen, Salt-Velocity Method of Measuring Water in Pipelines, *Engrs. and Eng.*, 39(6): 196-197 (1922).
11. J. Joly, On a New Method of Gauging the Discharge of Rivers, *Sci. Proc. Roy. Dublin Soc.*, New Series **16**(37): 489-491 (1922).
12. V. F. Hess, On the Use of a Radioactive Tracer Method in Water Measurement, *Trans. Amer. Geophys. Union*, **24**(Part 2): 587-594 (1943).
13. S. Karrer, D. B. Cowie, and P. L. Betz, Use of Radioactive Tracers in Measuring Condenser Water Flows, *Power Plant Eng.*, **50**(12): 118-120 (1946).
14. D. E. Hull, The Total-Count Technique: A New Principle in Flow Measurement, *Int. J. Appl. Radiat. Isotop.*, **4**: 1-15 (1958).
15. D. E. Hull, B. A. Fries, R. J. Dupzyk, and D. J. Lamoree, Isotope Engineering at Large Flow Rates, *Trans. Amer. Nucl. Soc.*, 3(2): 453-454 (1960).
16. D. E. Hull, Fluid Flow Measurement, U. S. Patents 2,826,699 and 2,826,700, Mar. 11, 1958; priority dates Oct. 29, 1954 and Apr. 27, 1956.
17. C. G. Clayton, The Measurement of Flow of Liquids and Gases Using Radioactive Isotopes, *J. Brit. Nucl. Energy Soc.*, **3**: 252-268 (1964). The article was also published in *Isotop. Radiat. Technol.*, **4**(2): 93-108 (Winter 1966–1967).
18. C. G. Clayton, Precise Tracer Measurement of Liquid and Gas Flows, *Nucleonics*, **18**(7): 96-100 (July 1960).
19. C. G. Clayton, A. M. Ball, W. E. Clark, and E. A. Spencer, The Accurate Measurement of Turbulent Flow in Pipes Using Radioactive Isotopes—The Isotope Dilution Method, in *Flow Measurement in Closed Conduits*, Conference Proceedings, East Kilbride, Scotland, 1960, Vol. 2, pp. 535-553, Her Majesty's Stationery Office, Edinburgh, 1962. (This work is also described in British Report AERE-R-3028, 1959.)
20. C. G. Clayton, W. E. Clark, and A. M. Ball, The Accurate Measurement of Turbulent Flow in Pipes Using the Isotope Velocity Method and the Effect of Some Restrictions on Optimum Operation, in *Flow Measurement in Closed Conduits*, Conference Proceedings, East Kilbride, Scotland, 1960, Vol. 2, pp. 555-576, Her Majesty's Stationery Office, Edinburgh, 1962. (This work is also described in British Report AERE-R-3090, 1959.)
21. C. G. Clayton, R. Spackman, and A. M. Ball, The Accuracy and Precision of Liquid Flow Measurement by Radioactive Isotopes, in *Radioisotope Tracers in Industry and Geophysics*, Symposium Proceedings, Prague, 1966, pp. 563-589, International Atomic Energy Agency, Vienna, 1967 (STI/PUB/142).
22. J. C. Schuster and R. L. Hansen, Discharge Measurements Using Radioisotopes in High-Head Turbines and Pumps at Flatiron Power and Pumping Plant, Colorado—Big Thompson Project, USAEC Report TID-25177, U. S. Bureau of Reclamation, December 1968.
23. J. C. Schuster and R. L. Hansen, Discharge Measurements Using the Radioisotope Velocity, Integrated Sample, Dilution and Total-Count Methods at Flatiron Power and Pumping Plant, Colorado—Big Thompson Project, USAEC Report TID-25185, U. S. Bureau of Reclamation, July 1969.
24. D. B. Smith, P. L. Wearn, and T. V. Parsons, Accuracy of Open Channel Flow Measurements Using Radioactive Tracers, British Report AERE-R-5676, June 1968.
25. C. G. Clayton and D. B. Smith, A Comparison of Radioisotope Methods for River Flow Measurement, in *Radioisotopes in Hydrology*, Symposium Proceedings,

XUM

Tokyo, 1963, pp. 1-24, International Atomic Energy Agency, Vienna, 1963 (STI/PUB/71).

26. D. E. Hull and M. Macomber, Flow Measurements by the Total-Count Method, in *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958,* Vol. 19, pp. 324-332, United Nations, New York, 1958.
27. D. E. Hull, Dispersion and Persistence of Tracers in River Flow Measurements, *Int. J. Appl. Radiat. Isotop.*, **13**: 63-73 (1962).
28. Half-lives and decay schemes are taken from F. E. McKinney, S. A. Reynolds, and P. S. Baker, *Isotope User's Guide,* USAEC Report ORNL-IIC-19, Isotopes Information Center, 1969.
29. Maximum permissible concentrations are taken from National Committee on Radiation Protection, *Maximum Permissible Body Burdens and Maximum Permissible Concentrations of Radionuclides in Air and Water for Occupational Exposure,* National Bureau of Standards Handbook 69, Superintendent of Documents, U. S. Government Printing Office, Washington, 1959.
30. D. B. Smith and W. E. Clark, An Investigation of the Hydraulics of an Underground Pool with Iodine-131, in *Radioisotopes in Hydrology,* Symposium Proceedings, Tokyo, 1963, pp. 77-88, International Atomic Energy Agency, Vienna, 1963 (STI/PUB/71).
31. W. J. Lacy and W. de Laguna, Method of Preparing Radioactive Cations for Tracing Groundwater, *Science,* **124**: 402 (1956).
32. G. Knutsson, K. Ljunggren, and H. G. Forsberg, Field and Laboratory Tests of Chromium-51–EDTA and Tritium Water as a Double Tracer for Groundwater Flow, in *Radioisotopes in Hydrology,* Symposium Proceedings, Tokyo, 1963, pp. 347-363, International Atomic Energy Agency, Vienna, 1963 (STI/PUB/71).
33. R. J. Heemstra, J. W. Watkins, and F. E. Armstrong, Laboratory Evaluation of Nine Water Tracers, *Nucleonics,* 19(1): 92, 94-96 (January 1961).
34. L. O. Timblin, Jr., and A. J. Peterka, Use of Radioisotopes for Open-Channel Flow Measurements, in *Radioisotopes in Hydrology,* Symposium Proceedings, Tokyo, 1963, pp. 37-61, International Atomic Energy Agency, Vienna, 1963 (STI/PUB/71).
35. E. Halevy, A. Nir, Y. Harpaz, and S. Mandel, Use of Radioisotopes in Studies of Groundwater Flow: Part I. Laboratory and Field Experiments on the Suitability of Various Tracers, in *Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1958,* Vol. 20, pp. 158-161, United Nations, New York, 1958.
36. R. E. Greene, Tracing with Activable Tracers. Part I, *Isotop. Radiat. Technol.*, 5(4): 269-277 (Summer 1968). Also, R. E. Greene, Tracing with Activable Tracers. Part II, *Isotop. Radiat. Technol.*, 6(1): 70-76 (Fall 1968).
37. R. P. Gardner and J. W. Dunn III, Stream Flow Measurement by an Inert Tracer Pulse Technique, *Nucl. Sci. Eng.*, **15**: 338-341 (1963).
38. M. Kobayashi and A. Nukazawa, Measurement of River Dilution and Flow by Means of Radioactive Tracers and Activation Analysis, in *Radioisotopes in Hydrology,* Symposium Proceedings, Tokyo, 1963, pp. 433-449, International Atomic Energy Agency, Vienna, 1963 (STI/PUB/71).
39. P. F. Berry, C. G. Clayton, and J. W. Webb, Tracer Study of Flow Characteristics in a High-Speed Gas Reaction Vessel by Means of ^{85}Kr, in *Radioisotope Tracers in Industry and Geophysics,* Symposium Proceedings, Prague, 1966, pp. 599-613, International Atomic Energy Agency, Vienna, 1967 (STI/PUB/142).
40. B. A. Fries, Gas Flow Measurements by the Total-Count Method, *Int. J. Appl. Radiat. Isotop.*, **13**: 277-280 (1962).
41. P. Johnson, Application of the Dilution Principle to the Measurement of Gas Flow Rates in Large-Scale Chemical Processes, in *Radioisotope Tracers in Industry and Geophysics,* Symposium Proceedings, Prague, 1966, pp. 615-624, International Atomic Energy Agency, Vienna, 1967 (STI/PUB/142).
42. G. Taylor, Dispersion of Soluble Matter in Solvent Flowing Slowly Through a Tube, *Proc. Roy. Soc. (London), Ser. A,* **219**: 186-203 (1953).
43. G. Taylor, The Dispersion of Matter in Turbulent Flow Through a Pipe, *Proc. Roy. Soc. (London), Ser. A,* **223**: 446-468 (1954).
44. J. Guizerix, discussion after paper by T. Dinçer, Applications of Radiotracer Methods in Streamflow Measurements, in *Isotopes in Hydrology,* Symposium Proceedings, Vienna, 1966, pp. 93-113, International Atomic Energy Agency, Vienna, 1967 (STI/PUB/141).
45. C. G. Clayton, A. M. Ball, and R. Spackman, Dispersion and Mixing During Turbulent Flow of Water in a Circular Pipe, British Report AERE-R-5569, May 1968.
46. C. G. Clayton, The Use of a Pump to Reduce Mixing Length in the Dilution Method of Flow Measurement, British Report AERE-R-4623, May 1964.
47. C. G. Clayton and G. V. Evans, Constant-Rate-Injection and Velocity Methods of Flow Measurements for Testing Hydraulic Machines, British Report AERE-R-5872, December 1968.
48. C. G. Clayton and R. Spackman, Improvements in or Relating to Injection Apparatus, British Patent 1,140,032, Jan. 15, 1969; priority date Jan. 20, 1965 (also U. S. Patent 3,477,461, Nov. 11, 1969).
49. D. V. Kniebes, P. V. Burket, and W. R. Staats, Argon-41 Measures Natural-Gas Flow, *Nucleonics,* 18(6): 142-144, 147 (June 1960).
50. A. E. Blake, Gas Meter Including Radioactive Apparatus for Metering Gaseous Fluids, Materials and Electrodes Sensitive to Gas Ionization, U. S. Patent 1,808,709, 1931. (*Chem. Abstr.*, **25**: 4389.)
51. B. Toudoire, Possibility of Gas Flow Measurements Using Ionization Produced by Radioactive Sources. Performance Obtained Using Continuous and Pulsed Ionization (in French), French Report CEA-R-3699, 1969.
52. C. G. Clayton and J. W. Webb, The Measurement of Mass Flow and Linear Velocity of a Gas by Continuous Ionization, *Int. J. Appl. Radiat. Isotop.*, **15**: 603-610 (1964).
53. G. L. Mellen, Velocity Metering of Gas Flow, U. S. Patent 2,611,268, Sept. 23, 1952; priority date June 2, 1947.
54. J. E. Lovelock and E. M. Wasilewska, An Ionizing Anemometer, *J. Sci. Instr.*, **26**: 367-370 (1970).

55. A. A. Obermaier, Ionization-Type Gas-Flow Meter, U. S. Patent 2,627,543, Feb. 3, 1953; priority date Nov. 12, 1947.
56. G. L. Mellen, Gas-Flow Speedometer, *Electronics*, 23(2): 80-81 (1950).
57. N. N. Shumilovskii and L. V. Mel'ttser, *Radioactive Isotopes in Instrumentation and Control*, pp. 129-135, The MacMillan Company, New York, 1964. (Translation from a Russian book published in 1959.)
58. C. G. Clayton and J. W. Webb, Continuous Measurement of Gas Flow Using a Hinged Gate and a Radioactive Source, in *Radioisotopes in the Physical Sciences and Industry*, Conference Proceedings, Copenhagen, 1960, Vol. I, pp. 499-509, International Atomic Energy Agency, Vienna, 1962 (STI/PUB/20).
59. N. N. Shumilovskii, Yu. V. Gushchin, and M. I. Tolokonnikov, The Utilization of Radioactive Isotopes for the Automatic Control of the Rate of Flow of Fluids, in Transactions of the All-Union Scientific Technical Conference on the Use of Radioactive and Stable Isotopes and Radiation in the National Economy and in Science, April 4–12, 1957, Moscow, Machine Building and Instrument Making, USAEC Report AEC-tr-4492, pp. 307-310; originally published in Russian by the Publishing House of the Academy of Sciences, USSR, Moscow, 1958.
60. R. Carlson, B. Cederberg, and K. Ljunggren, Measurements of the Water Circulation in a High-Pressure Natural-Circulation Boiler, *Combustion*, 33: 25-30 (June 1962).
61. J. F. Cameron, P. F. Berry, and F. Taylor, A Radioactive Method of Measuring Low Water-Flow Rates, *Brit. Chem. Eng.*, 4(2): 76-77 (1959).
62. W. R. Hencke and E. L. Cole, Radioactivity Flowmeter, U. S. Patent 2,714,168, July 26, 1955; priority date Dec. 29, 1951.
63. L. K. Hahn, Neutron Mass Flowmeter, Canadian Patent 842,963, May 26, 1970; priority date (U. S.) Jan. 24, 1966.
64. K. Ljunggren, Review of the Use of Radioactive Tracers for Evaluating Parameters Pertaining to the Flow of Material in Plant and Natural Systems, in *Radioisotope Tracers in Industry and Geophysics*, Symposium Proceedings, Prague, 1966, pp. 303-348, International Atomic Energy Agency, Vienna, 1967 (STI/PUB/142). [This paper was also published in *Isotop. Radiat. Technol.*, 5(1): 3-24 (Fall 1967).]

The Application of Nuclear Techniques to the Recovery of Faded Photographs

By R. M. Chatters and Camille Jacobs*

Supplementary Keywords: *industry, reproduction; activation, neutron; artifact; autoradiography; reactor; chlorine-36; nickel-63; copper-64; silver-108; silver-110m; iodine-131; mercury-203.*

Abstract: *Faded paper photographs, tintypes, and glass-plate negatives can be upgraded through neutron activation of the residual silver in the faded objects and subsequent exposure of photographic film or paper to the radiations from the long-half-life ^{110m}Ag so produced. The nuclear technique is presented as one method of faded-photograph recovery—not as the only or necessarily best method for so doing.*

Through chemical action and the ravages of time, many photographs have been threatened with discarding and destruction because the images have faded. The causes of fading are legion. Vestal[1] in a recent paper lists hydrogen sulfide, sulfur dioxide, rubber cement, water-absorbing glues and pastes, plywood, composition boards such as Masonite and Prestwood, newsprint papers, and sodium thiosulfate (hypo) among the chief culprits.

Fortunately a number of techniques have been developed to recover endangered materials of archival value. Recovery by direct photography and chemical treatment[2,3] has long been practiced; however, chemical recovery methods cannot always be applied without damage to the photographs. Thus a "nondestructive" technique was needed that would permit treatment without degradation or total destruction of the photographs requiring recovery. Ostroff[3-5] has reported that neutrons from a reactor were used to produce radioactive silver in photographic images and that autoradiographs were made from the activated photographs. The radiation emitted by the activated silver served the same purpose as other artificial radiant-energy sources or sunlight—to expose X-ray film from which a new negative was obtained. Ostroff reported that his sam-

*Radioisotope and Radiation Laboratory, College of Engineering Research Division, Washington State University, Pullman, Wash. 99163.

XUM

ples were activated for periods of from only seconds to minutes and that exposure to the film was limited to several minutes, with the exposure to film being made as quickly as possible after irradiation. With the assistance of Sayre,[6,7] Ostroff subjected a number of rare old (circa 1835–1840) photographs on which images were nearly completely gone to the neutron treatment. The clarity of the resulting new photographs was quite spectacular.

More recently Houtman[8] in the Netherlands has investigated the advantages of treating the image silver in photographic prints with radioactive solutions. He has reported that he obtained good results when he used solutions containing ^{203}Hg, ^{131}I, ^{63}Ni, ^{64}Cu, and ^{36}Cl. Some of his experiments showed that combinations of isotopes, such as ^{203}Hg and ^{131}I, lead to better results than either of the isotopes when used alone. Houtman felt that there were several advantages to his technique, i.e., "contaminants of the photographs have no influence and other isotopes than those of silver (hard β and γ emitters) can be used." Additional advantages lie in the fact that the investigator can more easily control the amount of radioactivity that is applied to the photograph.

Houtman's method has the same disadvantage that accompanies chemical recovery of photographs—through wetting, it may damage the paper print, cardboard backing, or, in the case of tintypes, the enamel coating.[9] However, the method should be very good for the recovery of large faded glass-plate negatives, which do not fit well into all reactor irradiation tubes.

For the past several years, Wagner[10] and his associates at Ohio State University have been experimenting with methods for the restoration of vintage 35-mm cellulose nitrate motion-picture film. The task is a formidable one. Wagner has considered the use of neutron activation recovery of the film but, because of the bulk of material to be treated, rejected the technique on the basis that "neutron activation would necessitate working with a mass of radioactive material beyond the limits of safety, time, and economic feasibility." For individual frames the technique would doubtless be of real service, but for full cans of film it appears at the moment to be impractical.

LONG-EXPOSURE METHOD

The approach to the problem of recovery of faded photographs by the present authors[9] differs essentially from that described by Ostroff in the length of irradiation and exposure times. Also, the Washington State University studies were extended to include tintypes, glass-plate negatives, and old documents. The results of research on old documents are not included in this article, but preliminary results show great promise.

Instead of a short irradiation time of the test photographs followed by immediate short exposures of photographs to film, optimum results on paper photographs (Figs. 1 to 4) were obtained when photographs were irradiated for periods up to 15 min at 10^{13} n/(cm^2)(sec). This was followed by storage of the "hot" photographs for up to 8 days and exposure of the film to the irradiated photographs for 24 hr. The most satisfactory film was Kodak Industrial X-Ray Type M. The principal reason for the difference in procedure was that, where Ostroff had his photographs exposed to the short-half-life (2.4 min) ^{108}Ag, in this work this short-half-life isotope was allowed to decay completely. Then the longer-half-life (260-day) ^{110m}Ag was used for exposure of the X-ray film. This delay procedure also eliminated the short-half-life radioisotopic forms of chlorine, bromine, and iodine, which were a matter of concern to Ostroff because of their presence in some photographs. These elements decayed very early and were not a problem in the Washington State University research, whereas, with the immediate-exposure technique of Ostroff and Sayre, they might affect the final product.

For most of the experimental work, old stereographic views, popular at the turn of the century, were found to be very useful because one of the pair of photographs served as the "control." The other photograph was irradiated in the reactor and used for making a new photograph. Thus comparison between a treated and an untreated photograph became more meaningful. Several examples of stereographs, even though not faded, were copied by means of neutron activation (Figs. 2 to 5). Each was activated at a flux of 10^{13} n/(cm^2)(sec) for 15 min and then exposed to X-ray film for 4 hr before developing. The activated photographs used to produce Figs. 1, 2, and 5 were stored for 7 days, that for Fig. 3 for 8 days, and that for Fig. 4 for 119 hr before exposure to the film. In each figure in this article, the photograph at the left shows the appearance of the original untreated photograph. With the exception of the tintype, each was a brown tone.

The most striking results (Fig. 6) of the research were obtained on a small tintype from which the image had become almost completely obliterated owing to having been wetted and scratched. This photograph was exposed in the nuclear reactor at a flux of 10^{13} n/(cm^2)(sec) for a period of 180 min, but, because of

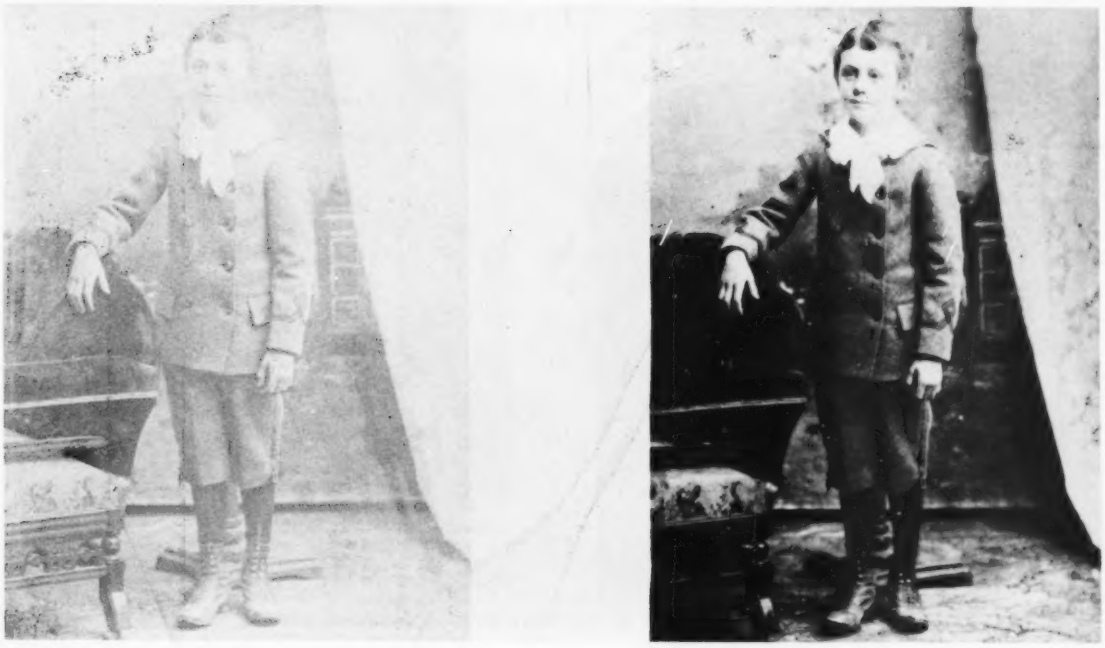


Fig. 1 "Standing Boy." Photograph on left irradiated with neutrons to produce photograph on the right.

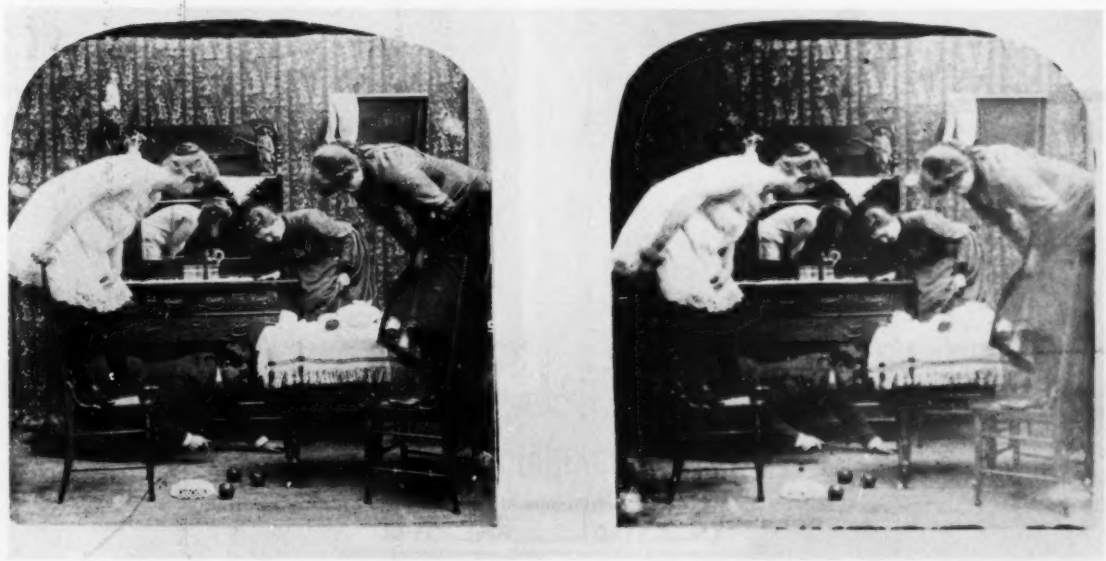


Fig. 2 "Biddie and the Rat." Stereograph (left) irradiated to produce photograph at the right.

XUM

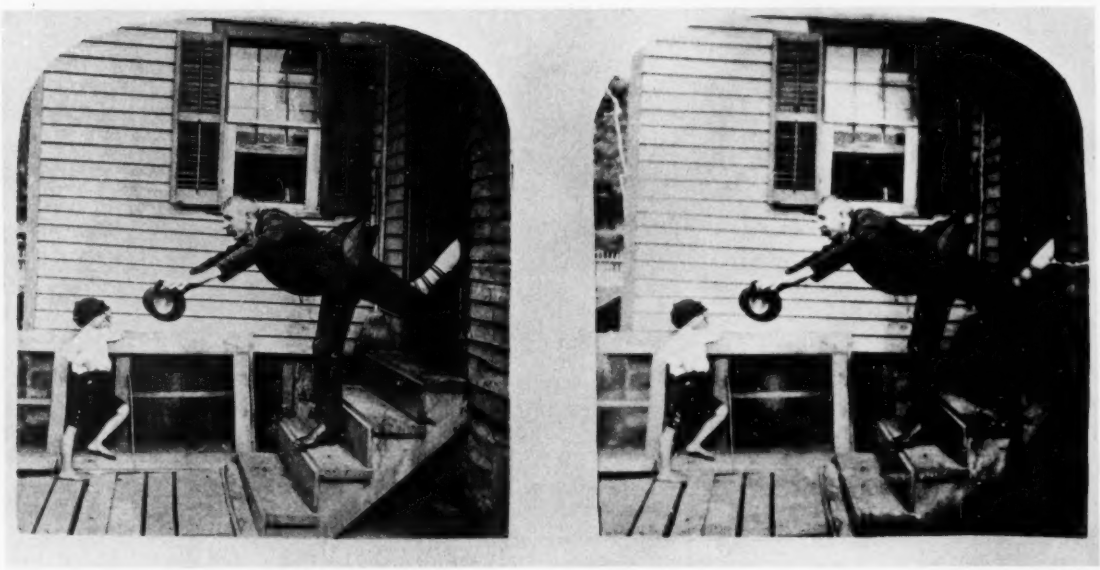


Fig. 3 "Hello Dad! What's the matter? You seem put out." Stereograph (left) irradiated to produce photograph at the right.

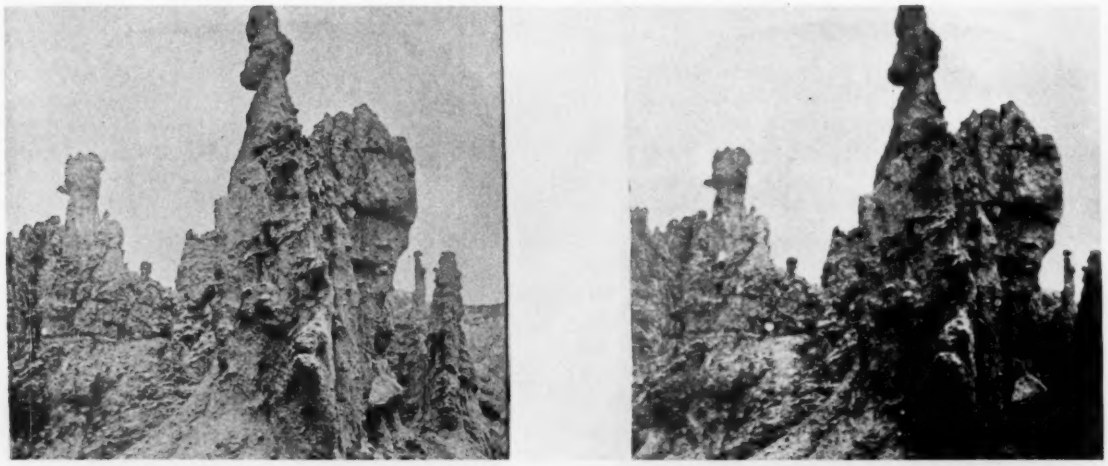


Fig. 4 "Basalt Field." Stereograph (left) irradiated to produce photograph at the right.

XUM

Fig. 5 "For heaven's sake, Maria, give us a rest!" Stereograph (left) irradiated to produce photograph at the right. Resulting photograph not equal in quality to the original.

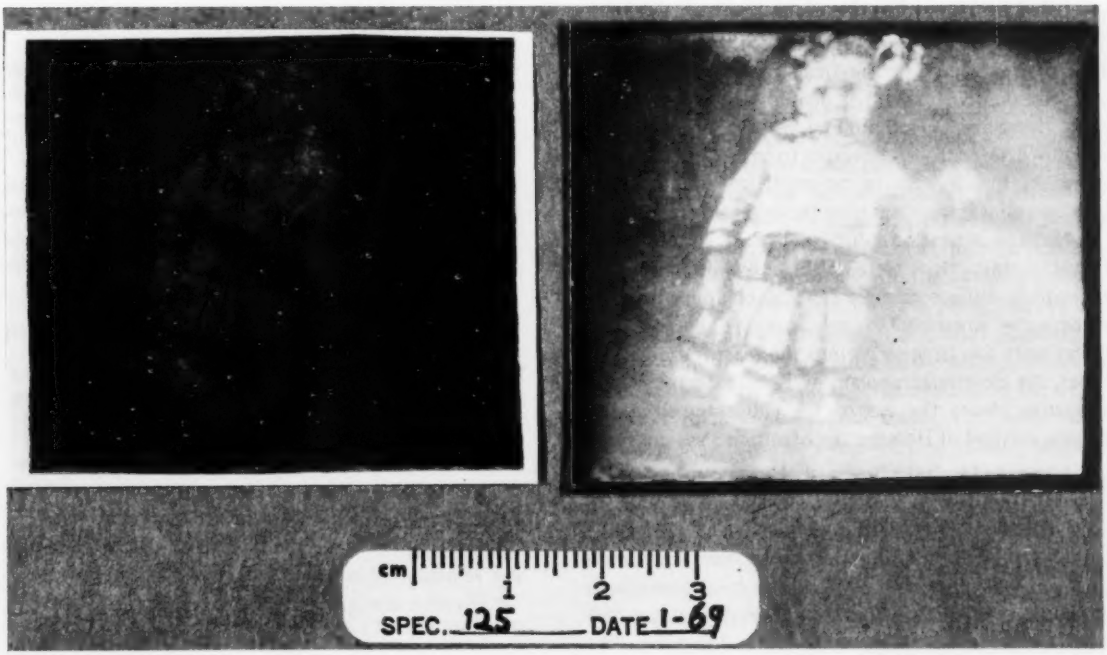


Fig 6 "Dr. Wilder's Mother." Faded and damaged tintype on the left was neutron-irradiated to produce photograph on the right.

XUM

the activation of the iron backing, the photograph was stored for 15 days before exposing the X-ray film to it for a period of 48 hr. This tintype was made about 90 years ago, as the subject of the photograph is now 94 years old. When presented with a copy of the upgraded photograph, she expressed her pleasure at seeing herself again in her "favorite dress."

The negatives produced from irradiated paper photographs are positive prints on film and require a second negative to be produced from them before paper prints can be made. On the other hand, a negative obtained following exposure of the film to an activated tintype is a true negative and can be used directly to produce a positive paper print. (The difference is that in a positive print the dark image is silver and in a tintype the dark image is the black enameled iron since such pictures are made by a reversal process.)

The autoradiograph contrast of prints could not be predicted. Each picture was a separate experiment in itself and required individual handling during exposure to photographic paper and subsequent development.

Further, as is shown in Fig. 2, intimate contact between all parts of the neutron-activated photograph and the X-ray film was often difficult to accomplish. Where close, uniform contact between the activated photograph and the X-ray film was not possible because of an uneven (wrinkled or folded) photograph, lack of uniformity in the final image resulted. With tintypes that were bent or dented—as was the case with the tintype used in Fig. 6—the problem was magnified severalfold. Attempts to upgrade the stereograph in Fig. 5 were to no avail; in fact, the new photograph was less clear than the original.

Neutron activation of a faded glass negative produced results that were sufficiently promising to indicate that this technique can also be applied to the recovery of these old plates. However, because the plates were too large to go into the reactor irradiation tubes, the experimental plates were cut into 1- by 2-in. segments. Hence the use of the radioactive-solution-tagging method of Houtman or of a tunnel system such as has been available to Sayre for neutron activation at the Brookhaven National Laboratory would be more suitable for the recovery of old plate negatives.

During the course of the research, a number of experiments were carried out to determine the feasibility of going directly from the irradiated photograph to photographic paper. The results indicate that this technique can also be used for the recovery of faded paper photographs. The method of direct exposure of photographic paper to irradiated tintypes and glass-plate negatives has not yet been attempted.

(RHL)

REFERENCES

References marked with an asterisk have not been verified by the editors; for further explanation, see the Foreword.

1. *D. Vestal, Are Your Prints Fading Away?, *Pop. Photogr.*, **64**(4): 67-68, 106-109 (1969).
2. *Restoring Faded Photographs, *Defender Trade Bulletin*, Defender Photo Supply Co., Inc., Rochester, N. Y., circa 1940.
3. E. Ostroff, Talbot's Earliest Extant Print, June 20, 1835, Rediscovered, *Photogr. Sci. Eng.*, **10**: 350-354 (1966).
4. E. Ostroff, Early Fox Talbot Photographs and Restoration by Neutron Activation, *J. Photogr. Sci.*, **13**: 213-227 (1965).
5. E. Ostroff, Restoration of Photographs by Neutron Activation, *Science*, **154**: 119-123 (1966).
6. E. V. Sayre, Revelation of Internal Structure of Paintings Through Neutron-Activation Autoradiography, in Proceedings of the First International Conference on Forensic Activation Analysis, San Diego, Calif., pp. 119-132, Gulf General Atomic Incorporated, 1966.
7. E. V. Sayre, Nuclear Age and the Fine Arts, in Proceedings of the 1967 Youth Congress on the Atom, USAEC Report BNL-12314, 1967.
8. J. P. W. Houtman, personal letter to R. M. Chatters, February 1969.
9. R. M. Chatters and Camille Jacobs, Recovery of Faded Photographs by Nuclear Techniques, *Photogr. Appl. Sci. Technol. Med.*, 4(15): 26-27, 47 (1970).
10. *R. W. Wagner, Preservation and Restoration of Photographic Materials Through Nuclear and Ultrasonic Methods, presented at the Second Annual Indiana–Kentucky Archives Seminar, Louisville, Ky., Apr. 24, 1970.

Labeling of Copper Wire with ^{110m}Ag for Subsequent Identification

By L. C. Bate and F. F. Dyer*

Supplementary Keywords: *forensic investigation, material tracing differentiation*

Abstract: *Labeling of copper electric cable with ^{110m}Ag was demonstrated as a suitable technique for use in subsequent identification of such cable in case of theft. The ^{110m}Ag, in solution, is applied inside the cable, i.e., on the surfaces of the wires that are twisted together to form the cable, with a hypodermic needle and allowed to dry. The label is not removed by several years of simulated weathering and can be detected by monitoring with a survey-type radiation meter. The technique can be carried out by a semiskilled person with a minimum of training.*

Copper wire stolen from storage areas of power companies and remote power lines is difficult to identify even if subsequently located. The stolen wire may even be cut into pieces 1½ to 3 ft long, burned to simulate scrap, and sold to a junkyard. Therefore a permanent label, which will not be detached under weathering conditions or when the wire is burned, is needed together with an easy, rapid identification method for the label at such time as the labeled wire may be located.

A radioisotope that may be readily attached to copper wire and later identified by a survey meter appeared to offer promise as a label. The technique of applying such a label, its permanence after being applied, and a method for identifying it later were thus investigated.

PROCEDURE

Since copper wire may not be stolen for some time —several months to a year after being labeled— the half-life of the radionuclide used should be fairly but not excessively long, and a radionuclide with a half-life of about 1 year was decided on. For detection of the radioactive label in a pile of scrap, the radionuclide should be one that emits energetic gamma rays and preferably a large number of gammas per disintegration. The nuclide ^{110m}Ag was selected because it (1) has a desirable half-life ($T_{½}$ = 270 days), (2) emits eight gamma rays with energies exceeding 600 keV and branching ratios exceeding 10%, and (3) has chemical properties such that its ions tend to be readily reduced and form a stable deposit on copper. The nuclides ^{106}Ru and ^{192}Ir were also considered but thought to be less suitable than ^{110m}Ag.

Because size 000 wire—37 strands of wire twisted into a ¾-in.-diameter cable—is the most often stolen, work was concentrated on this material. A few tests were made on single-strand wire of ⅛ in. diameter.

Labeling Technique

About 0.2 ml of solution is placed between the strands of a copper cable so that the liquid flows into the air space inside the cable. The rate of penetration of liquid between the strands was found to depend on the acidity of the solution. A solution of 0.5*M* HNO_3 appeared to give optimum deposition. The radioactive tracer was diluted to 100 μCi/ml and adjusted to 0.5*M* acidity. This solution was introduced between the strands of the cable with either a disposable pipet or a hypodermic needle. Usually the solution was simply allowed to dry in order to deposit the ^{110m}Ag, but sometimes formaldehyde was added to enhance deposition. Electrodeposition was also tested. The electrical potential was applied by attaching the negative terminal of a 6-V battery to the cable and the positive terminal to a wire in contact with the solution inside a disposable glass pipet, the solution being allowed to run gradually between the cable strands. In labeling a large amount of cable, injection of the labeling solution would be repeated at specified intervals along the wire.

After the solution had dried, the cable was lacquered with Sherwin-Williams clear lacquer No. AA 13505, which is specifically made for coating copper and is phosphorescent under certain types of light. The radioactivity in the cable was measured, the cable wiped with a damp cloth, and the radioactivity remeasured to determine the amount removed. When thoroughly dry, the cable was flushed with water again and recounted. To test the permanence of the label under simulated field and weathering conditions, the cable was placed in the south window of a laboratory, where it stayed in the sunlight for a year and a half,

*Analytical Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn. 37830.

XUM

after which it was wiped, and both wipe and cable were recounted. The cable was then flamed with a burner to simulate burning and flushed with water, radioactivity measurements being made after each of these procedures.

In the field tests, a Victoreen survey meter 3 ft from the cable in a scrap pile was used for detecting 45 μCi of ^{110m}Ag.

(Table 3). The "as-is" wire had an oxide film, which was in some cases cleaned by sanding. In half the tests formaldehyde was added to reduce the silver ion on the copper wire and improve the bonding.

Field Test. A field test using 45 μCi of ^{110m}Ag plated on a copper wire was performed to demonstrate the ability to locate the radioactive label in a pile of

Table 1 Permanence of ^{110m}Ag Label on Copper Cable

Material tested	HNO_3 conc. in deposition solution, *M*	^{110m}Ag remaining, % of deposited			
		After 1st wash	After 2nd wash	After burning	After 3rd wash
Cable A	0.1	96	92	92	85
Cable B	0.1	99	94	94	89
Cable C*	0.5	106	105	109	108
Cable D	0.5	93	94	96	96
Cable E	0.5	96	96	99	98
Average†		98^{+8}_{-5}	96^{+9}_{-4}	98^{+11}_{-6}	95^{+13}_{-10}

*Values consistently >100% probably owing to errors in positioning the cable 30 cm above the detector (see Table 2).

†Error values show the range for the five cables.

RESULTS

In five tests (as described above) on 37-strand copper cable, ^{110m}Ag losses averaged 4.5% (7.6% if the high values for test C are excluded) (Table 1). Sunlight, by reducing the ^{110m}Ag ions to metallic silver, should improve the bonding of the tracer to the cable. An HNO_3 concentration of 0.5*M* in the deposition solution resulted not only in better deposition but also in better retention than did 0.1*M*.

Turning the cable on its horizontal axis, with the same side of the cable facing the detector, resulted in changes in the count rate (Table 2). This apparently is due to changes in the amount of radiation that can be "seen" by the detector through the cracks between the strands, since after being heated the cable tends to unwind slightly, leaving larger cracks between the strands than before. Because the tracer is coated on interior surfaces, the angle to the counter apparently has a large effect on the count rate observed.

In a few tests on single strands of wire, after deposition of the tracer on the surface of the wire under several conditions, the wires were damp wiped to determine the amount of ^{110m}Ag that would remain after handling, as would occur in installation. As would be expected, retention was rather poor but was markedly improved by application of a lacquer coating

Table 2 Count-Rate Variation with Horizontal Rotation of Copper Cable

Change in angle, deg	Count rate, counts/min	Change in angle, deg	Count rate, counts/min
0	374,579	100	332,225
20	361,995	120	358,588
40	347,170	140	379,285
60	326,076	160	378,384
80	322,701	180	377,301

Table 3 Retention of ^{110m}Ag on Surface of Single Strands of Wire After Damp Wiping

Wire	^{110m}Ag remaining after wiping, % of deposited	
	No lacquer	Lacquered
As is	43.4	68.7
Sanded	63.9	83.6
Formaldehyde used in ^{110m}Ag deposition		
As is	46.8	83.6
Sanded	68.2	82.1

XUM

copper scrap. The ^{110m}Ag source was placed under a pile of copper scrap. When the area was monitored with a Victoreen radiation instrument, it was possible to detect the radioactive material at about 3 ft. This should be an extreme case since in actual practice the labeled material should be distributed throughout the pile rather than at the bottom. Each label would contain 20 μCi of ^{110m}Ag, and a pile of scrap would likely have several labeled pieces. Of course, scanning at a distance closer than 3 ft would probably be possible. With careful monitoring of a scrap pile, the presence of one piece of labeled scrap should be detected.

SAFETY

The radioactive tracer can be applied to the copper by a person with a minimum amount of training in the handling of radioactivity, the proper solution being made up in the laboratory prior to the labeling operation. (MG)

Radioisotopic X-Ray Gage for Determining Particle-Size Distributions*

Supplementary Keywords: *measurement and control system; industry; source, X-ray; promethium-147.*

A radioisotopic gage for determining weight-size distribution of particles in the solid phase of a suspension has been designed and tested. Such an instrument is needed for use in powder technology to give the weight distribution of powder samples in suspension quickly and reliably. The new instrument, which is simple to operate and economic in cost, hopefully will fill this need for a wide variety of powders. Because of the constancy of the X-ray beam, corrections do not have to be made for source-intensity variations during operation.

The instrument (Fig. 1) contains a ^{147}Pm X-ray source and a proportional counter, located on opposite sides of a settling tank. The intensity of the transmitted X-ray beam, determined by the counter, is proportional to the weight fraction of particles smaller than the Stokes' diameter applicable to the time and depth of fall. Hence the cumulative weight percentage of undersize particles is obtainable from the intensity readings.

In operation, the intensity of the transmitted beam is determined first with clear liquid in the tank, and then the powder under study is added and the suspension stirred. The sedimentation rate is determined by scanning the tank, moving the source and

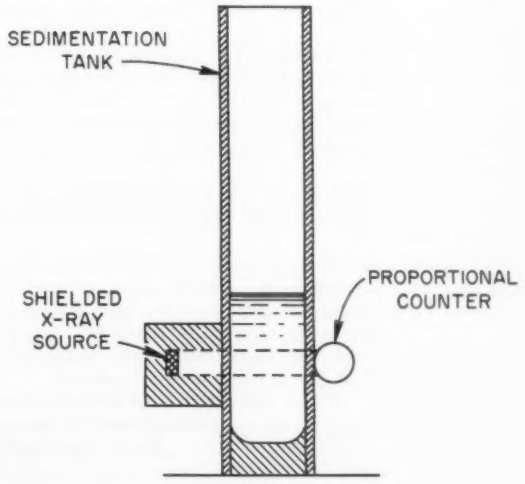


Fig. 1 Promethium-147 X-ray gage for determining sizes of suspended particles.

counter upward (by a small electric motor) during a preset time that depends on the material under study. The graph obtained, of time vs. intensity, is converted to X-ray density (i.e., log of intensity), which is proportional to the powder concentration. The X-ray density for several materials with particles of micro-meter dimensions was shown to vary linearly with concentration of the material in the range 0.1 to 1.0 vol.%. Values were reproducible with bronze powder in cyclohexanol and in 50% glycerol–water.

*Summary of "A New X-Ray Sedimentometer," by T. Allen and L. Svarovsky, *Journal of Physics, E. (London)*, 3: 458-460 (1970).

XUM

In the experimental setup used, the sedimentation tank was made of a high-quality Perspex, and the windows (for beam definition), of lead. Except for the brass source and detector holders, the rest of the equipment was of stainless steel. The proportional counter (1300 V) was xenon-filled.

The principle of this gage is similar to one developed under contract to the USAEC Division of Isotopes Development for determining the amount of sediment suspended in a flowing stream [*Isotopes and Radiation Technology*, **4**(4): 358-362 (Summer 1967)]. (MG)

A SIMPLE NEUTRON RADIOGRAPHY SET*

Supplementary Keywords: *source, neutron; economics; industry; californium-252.*

Useful-quality neutron radiography with a very small neutron source of ^{252}Cf (140 μg) has been described. The USAEC, who sponsored its development, hopes eventually to provide ^{252}Cf at a cost of 50 cents per microgram. The ancillary equipment is simple—a bucket of tap water, some small sheets of metal foil, a cassette, and a box of X-ray film. The radiograph of a combination lock (Fig. 1) is typical; it

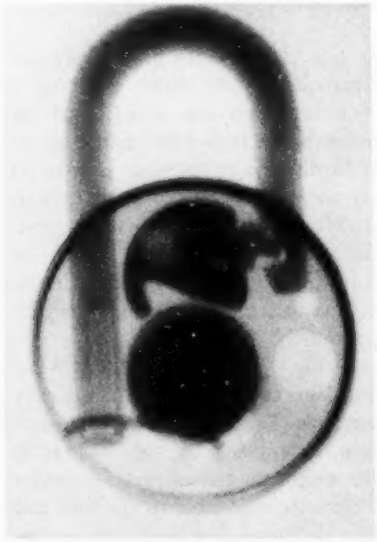


Fig. 1 Radiograph of a combination lock. [From *Materials Evaluation*, 27(12): 12A (1969).]

shows clearly the combination mechanism of the lock. Coarse-grained radiographs require only a 20-min exposure; fine-grained radiographs may require overnight exposure. With a small investment (<$300), any manufacturer should someday soon be able to have his very own radiography set—one that is simple and safe and requires little attention. Foreseeable uses of ^{252}Cf as a neutron source have been discussed earlier in this journal.† (HPR)

*From J. P. Barton and M. F. Klozar, Your Own Personal Neutron Radiography Set, *Materials Evaluation*, 27(12): 12A (1969).

†J. P. Barton, Foreseeable Application of ^{252}Cf to Neutron Radiography, *Isotopes and Radiation Technology*, 7(3): 285-291 (1970).

XUM

^{13}C HELPS REVEAL CARBOHYDRATE STRUCTURE*

Supplementary Keywords: *chemistry, organic; biology; tracer; molecular structure; reaction mechanism; data handling; enriched stable isotope use; economics.*

Carbon-13 nuclear magnetic resonance (NMR) spectroscopy is being used to study carbohydrate structure. A. S. Perlin and B. Casu with H. J. Koch at McGill University, Montreal, are pioneering the work. Improvements in instrumentation have overcome problems associated with the low natural abundance (1.1%) of ^{13}C. This stable isotope is a valuable tracer for organic-mechanism and biological studies, and ^{13}C-NMR data are an important addition to proton-NMR data. If the demand increases for ^{13}C-enriched chemicals to be used in such work, their current high cost may decrease.

The aspects of carbohydrate ^{13}C-NMR spectroscopy being studied by Dr. Perlin and associates include chemical shifts, delocalization, substituent effects, interaction energy, chemical reactivity, and orientation of substituents. Spectrums are measured at 25.15 MHz and are time-averaged by computer to obtain average signals from many scannings of ^{13}C in its natural abundance.

In studies of chemical shifts typified by work with the anomers α- and β-D-glucopyranose (glucose), it was learned that change of OH-1 from an equatorial orientation in the β-anomer to an axial orientation in the α-anomer causes increased shielding of most carbons in the molecule, an effect that is accompanied by decreased shielding of the appended protons. This interaction causes changes in bond polarization throughout the molecule.

These readjustments of electron density delineate a strain-delocalization process in response to steric compression caused by the axial hydroxyl group. The NMR spectrums reflect the result as a change in the ^{13}C and proton chemical shifts on going from the equatorial to the axial orientation. The data taken for carbohydrates indicate that the dependence of chemical shift on structure follows generally understandable patterns and corresponds closely with the findings by others of ^{13}C shielding and ^{1}H deshielding effects for isomeric cyclohexane derivatives.

Perlin's study of the influence of numerous functional groups and substituents on ^{13}C chemical shifts of carbohydrates showed that electronic effects are very prominent and generally conform to those expected from the behavior of other classes of compounds.

In considering interaction energy, Perlin proposes that the relative stabilities of isomeric compounds should be reflected in their ^{13}C chemical shifts; that is, if overriding polar influences are absent, the experimentally determined shifts should be a measure of energy differences of steric origin. He and his associates have shown for a number of sugars that energy differences between anomeric and diastereomeric sugars, or between geometric and positional isomers of cyclohexanes, parallel the relative overall shielding states of their ^{13}C nuclei. He suggests that ^{13}C and other chemical-shift data may aid in assessing the relative contributions of repulsive and stabilizing interactions within molecules.

Electron-density and bond-polarization changes revealed by ^{13}C-NMR spectroscopy should permit comparison of sugar chemical reactivity as a function of electronic ground states.

Proton spin–spin splitting of ^{13}C is found to depend markedly on orientation of substituents. For example, the axial H-1 β-glucose couples only with the appended ^{13}C-1, whereas the equatorial H-1 of the α-anomer couples to at least two other ^{13}C nuclei. Therefore long-range C–H coupling may be an independent criterion for conformation.

It appears that ^{13}C-NMR spectroscopy should become increasingly important in the study of the structure and stereochemistry of carbohydrates. (HPR)

*Condensed from "Carbon-13 NMR Gives Sugar Stereochemistry," *Chemical and Engineering News*, June 8, 1970, pp. 78–79.

XUM

RADIOGRAPHY USING PHOTONUCLEAR REACTION*

Supplementary Keywords: *autoradiography; activation, photon; comparison; Japan.*

A method of radiography developed at the Radiation Center of Osaka Prefecture using the photonuclear reaction eliminates the scattered photons generated in the sample. A metal plate is placed at the position occupied by the X-ray film in ordinary radiography, and the object is irradiated with high-energy gamma or X rays. The metal plate is activated only by the components of energy higher than the photonuclear threshold, and scattered photons do not affect the metal plate. After the irradiation, a film is placed in contact with the metal plate for a time and developed by autoradiography techniques like those in neutron radiography. The contrast and definition of the picture were shown to be much better than those in ordinary radiography. (MG)

*Abstract of article (in Japanese) by Junichiro Furuta and Eiichi Hiraoka in *Journal of NDI (Hihaki Kensa)*, 17(3): 99-104 (1968).

THE CARBON-14 DATING OF IRON

By N. J. van der Merwe,* The University of Chicago Press, Chicago, 1969 (137 pp., $7.00, hardback).

Supplementary Keywords: *metallurgy, ferrous; artifact; geophysics; material tracing; technique; history; theory, applied; thesis; bibliography.*

Not often is the interrelation of diverse disciplines presented so intriguingly as in *The Carbon-14 Dating of Iron*. The isotope ^{14}C binds together archaeology, history, metallurgy, and chemistry in this short and fascinating account of Professor van der Merwe's doctoral thesis research at Yale. By text and chart, the significance of the role of carbon in iron metallurgy is presented vividly. The reader comes to feel conversant with the differences among bloomery iron, wrought iron, cast iron, and steel and then to understand how treasures came to be—such as Merovingian and Viking swords, whose surface texture creates an impression of light and dark bands, or Damascus blades, which have a surface like watered silk. Interesting historic facts are revealed—one of man's earliest sources of iron was of extraterrestrial origin (meteorites); iron was once 40 times as valuable as silver.

The significance of Dr. van der Merwe's research is that it resulted in the successful development of a method for the ^{14}C dating of iron artifacts prepared with charcoal (coal contains no ^{14}C) and also demonstrated the applicability of ^{14}C measurements to the dating of iron slag and of copper slag as well. The technique is a means to knowledge about the types of ores, fuels, and reducing agents used throughout history in iron metallurgy. In lieu of a charcoal specimen, an iron specimen may be equally valuable to an archaeologist; in lieu of both, a slag specimen may be just as useful. For the metallurgist, knowledge of the fuel and flux involved in the smelting operation, as well as of the slag produced from it, is essential in reconstructing the metallurgical process. For the historian, the history of fuels used in iron metallurgy and the history of charcoal production can be deduced from the ^{14}C data.

Professor van der Merwe describes the method in detail and, among his data, presents interesting results from Iron Age archaeological sites. (HPR)

*Assistant Professor of Anthropology, State University of New York, Binghamton.

Section III

Isotopes and Radiation Technology

Food Irradiation

Study of Irradiated-Pasteurized Fishery Products*

By L. J. Ronsivalli, F. J. King, V. G. Ampola, and J. A. Holston†

Supplementary Keywords: *food preservation; seafood; modification, material; food evaluation, subjective; industry, food; industry; bibliography.*

Abstract: *The results are given of a study of the maximum shelf life of irradiated and nonirradiated commercial-grade cod fillets, prime-quality haddock fillets, and prime-quality pink and brown shrimp. The increase in shelf life provided by irradiation is inversely proportional to the storage temperature. Gas chromatography was used to study the effects of radiation or storage, or both, on the chemical composition of cod and haddock fillets and to assess the similarity in chemical composition between irradiated and nonirradiated fish of both species.*

This article briefly summarizes research on radiation pasteurization of seafood conducted by the Bureau of Commercial Fisheries, Technological Laboratory, Gloucester, Mass., for the USAEC from Oct.1, 1960, to Sept. 30, 1967. Detailed results are given for the research conducted from Oct. 1, 1967, to Sept. 30, 1968. The early work included the determination of the feasibility of radiopasteurizing various commercially important marine species; more recent work has been aimed at acquiring data needed to obtain approval from the Food and Drug Administration (FDA) to market irradiated seafood.

RESULTS OF THE PAST WORK

Radiopasteurization of haddock, cod, pollock, ocean perch, and soft-shell clams is technologically feasible. Lobster, mackerel, scallops, and blue crab are also amenable to radiopasteurization. Radiation doses in the 150- to 450-krad range doubled or tripled the refrigerated shelf life of these products. Storage temperature has some effect; irradiated fish had a shelf life of 1 month or greater at 33 to 35°F (0.5 to 1.7°C) but only 2 weeks at 42°F (5.5°C). For irradiation, as well as for any preservation technique, the better the pretreatment quality of the product, the longer the shelf life.

Irradiation also extends the shelf life of fish that has already been stored in ice for a substantial portion of its normal shelf life. Nonirradiated fish stored at sea for 7 days in ice can be kept no more than 7 additional days on shore, but, if they are irradiated when the boat is unloaded, the fish can be kept up to 2 or 3 times as long.

The organoleptic acceptability of radiopasteurized haddock and cod fillets has been tested with large groups of people, including panels of several hundred soldiers at a military post and of up to 100 people at scientific meetings.[1] Radiation effects on amino acids and B vitamins in seafood are relatively insignificant—certainly no greater than the effects of seasonal variations.[2,3]

Many of the FDA-approved materials for packaging irradiated food were found to be suitable for packaging radiopasteurized fish; best results are obtained with materials having excellent gas-barrier properties. All the packaging materials tested are effective barriers to bacteria.[4] Clams, which are susceptible to oxidative browning, and ocean perch, which are susceptible to rancidity, store better when vacuum packaged.

Gas-chromatographic and classical wet-chemistry methods were used to follow changes in the volatile compounds from nonirradiated and irradiated fish. Radiation caused immediate increases in carbonyl

*L. J. Ronsivalli, F. J. King, V. G. Ampola, and J. A. Holston, Study of Irradiated Pasteurized Fishery Products, USAEC Report TID-25312, Bureau of Commercial Fisheries, April 1970.

†Bureau of Commercial Fisheries, Technological Laboratory, Gloucester, Mass.

XUM

concentrations in the presence of oxygen, but the volumes of these compounds did not exceed those volumes reached as a function of storage only. Production of sulfides was inhibited by irradiation. No aberrant compounds were found in volatile substances from irradiated fish.[1]

Irradiation at pasteurization levels (150 to 250 krads) reduces the microbial population 2 to 3 log cycles as determined by total plate count.[5] By the time irradiated fish become organoleptically unacceptable, total plate count may be as high as 10^8 or 10^9 microorganisms/g, which is relatively high; nonirradiated fish may have a total plate count of 10^6 to 10^7 microorganisms/g at spoilage. The difference may result from differences in the biochemical activities between common spoilage organisms and organisms that survive irradiation.

The composition of microflora in fish was altered significantly not only by irradiation but also by packaging the fish in hermetically sealed containers.[6,7] These two techniques appear to complement each other because a lower radiation energy is required to preserve vacuum-packed fish than is needed for air-packed fish.

Data[1] have been obtained on heat penetration of haddock fillets during cooking and on heat inactivation of the toxin of *Clostridium botulinum* Type E. Results indicate that normal cooking readily destroys the toxin. Sodium nitrite and sodium tripolyphosphate can be absorbed by fish fillets[8] in amounts sufficient to inhibit growth of *C. botulinum* Type E.

MAXIMUM SHELF-LIFE STUDY

Despite the tremendous amount of past work, evidence is still needed that radiopasteurized fish undergo spoilage just as nonirradiated fish do, even though the former do take longer to spoil. Data are also needed for assessing the potential hazard of *C. botulinum* Type E. Radiation destroys the common fish spoilage microorganisms and thereby extends product shelf life; this effect might create a situation favorable for the growth and toxin production of *C. botulinum* Type E. Spoilage must occur before any possible botulinum toxin development. A program has been initiated to determine the maximum shelf life of nonirradiated and irradiated haddock and cod fillets because these data have direct bearing on spoilage and *C. botulinum* hazards.

Some research into this problem was reported previously.[9] In addition to haddock and cod fillets, pink shrimp and brown shrimp were also investigated.

Maximum shelf life is defined as the period, in days, after which a product stored at a particular temperature is rejected unanimously on the basis of odor alone by an untrained panel of at least 20 consumers. The term "X value" is used to denote maximum shelf life. An expert panel also determined maximum shelf life. A comparison of the two panels' results should reveal any radiation-induced alteration in seafood that might bias an untrained panel. No such bias was found.

Cod

Experiments were completed with irradiated and nonirradiated commercial-quality fillets cut from 2- to 4-day old cod that were caught and handled under ordinary conditions. Cellophane-wrapped fillets were separated into four lots for irradiation at doses of 0, 75, 100, and 200 krads. Each lot was subdivided for storage at 38, 42, 48, and 55°F (3.3, 5.5, 8.9, and 12.8°C). Samples were presented to the expert panel in loosely capped 1000-ml beakers. Two or more samples of known ages were included in each test. After each lot was rejected by the expert panel, it was submitted to the consumer panel (personnel of the Bureau of Commercial Fisheries, Technological Laboratory). The untrained panel was also presented with good quality samples to check the accuracy of the response of the untrained panelists. All samples eventually spoiled, of course. Results of the experiments (Table 1) show that nonirradiated fish become unacceptable within a rela-

Table 1 Maximum Shelf Life of Irradiated and Nonirradiated Commercial-Quality Cod Fillets

Dose, krads	Exp.	X value, days: Storage temp., °F 33	38	42	48	55
0	1		11	8	7	4
	2	14	11	7	7	3
	3	12	11	7	5	4
75	1		11	11	10	7
	2	23	18	9	8	7
	3	40	27	9	11	6
100	1		15	11	11	9
	2	30	21	15	10	8
	3	49	30	15	12	6
200	1		30	23	15	10
	2	45	32	22	14	8
	3	50	29	22	13	9

tively narrow range of time at each storage temperature. However, irradiated samples differ from each other, especially at the lower temperatures and higher doses. This finding indicates that the extra-long shelf-life extensions occur at temperatures at which botulinum toxin cannot be produced (<38°F). Since irradiation is most effective at lower storage temperatures, commercial handlers will be financially motivated to maintain low temperatures.

Haddock

One X-value experiment was completed on prime-quality skinless haddock fillets. The results (Table 2) are similar to the cod data.

Table 2 Maximum Shelf Life of Prime-Quality Skinless Haddock Fillets

Dose, krads	X value, days Storage temp., °F 38	44	46	50
0	14	7	7	4
50	19	14	9	9
100	24	15	16	10
200	35	18	17	15

Shrimp

Pink shrimp and brown shrimp, caught off Florida, were packaged in polyethylene-coated polyester pouches, with headspace volume minimized by the packager's pushing out the air before heat-sealing the pouch. At irradiation, the brown shrimp were 2 days and the pink shrimp 4 days out of the water.

All samples developed the characteristic spoilage odors of shrimp; brown shrimp became discolored, and nonirradiated brown shrimp developed black spots. The brown shrimp had longer X values than did the pink shrimp (Tables 3 and 4); however, the X values of the two species were almost the same at the 200-krad dose. As with the cod and haddock fillets, the effectiveness of radiation as a preservative was greater at lower storage temperatures.

Toxin Outbreak

Proper evaluation of the safety of radiopasteurized fish requires information on toxin outbreak times as well as information on X values. The minimum time required for production of toxin in seafood inoculated with *C. botulinum* and stored under conditions similar to those used for X-value determinations is necessary. The inoculation level should be sufficiently higher than the normal incidence level to provide a safety factor. Microbiologists at the Massachusetts Institute of Technology conducted a survey[10] which showed that the incident level of *C. botulinum* Type E is very low—0.17 microorganism/g. A safety factor of 1000 would mean that there would be recognizable spoilage well in advance of toxin production in a sample inoculated with 170 microorganisms/g.

Table 3 Maximum Shelf Life of Irradiated and Nonirradiated Brown Shrimp

Dose, krads	X value, days Storage temp., °F 38	42	48	55
0	15	13	6	3
50	27	15	8	9
100	35	24	10	8
200	30	27	10	10

Table 4 Maximum Shelf Life of Irradiated and Nonirradiated Pink Shrimp

Dose krads	X value, days Storage temp., °F 33	37	42	48	55
0	17	10	10	5	2
50	27	20	12	6	4
100	28	25	12	10	6
200	44	33	26	13	7

RADIATION EFFECT ON CHEMICAL COMPOSITION OF COD AND HADDOCK

Considerable progress has been made in developing the technology of radiation preservation of seafood, but there is a need to establish that consumption[11] of irradiated seafood is safe. Some animal feeding studies have been completed and more are planned; however, basic information on the chemical effects of ionizing radiation on seafood is needed to evaluate these studies and to plan further studies. Most of the knowledge

XUM

about effects of radiation on organic compounds has been gained from studies of simple systems of known components.[12] Some model-system studies have been oriented toward foods,[13] and some work has been done on irradiated foods.

The rationale of the experimental procedures used in this study is that ionizing radiation has the potential to induce oxidative reactions in muscle and to fragment a wide variety of chemical compounds in situ. Chemical or physical methods are used to extract[14] chemical components from fish fillets; the extracts are then analyzed by gas chromatography. Nonvolatile extractable components are converted to volatile derivatives, which are also analyzed by gas chromatography.

Packaging, irradiation, and storage procedures used in this study were based on requirements for the petition to FDA for approval to market irradiated seafood. Two "sterilizing" doses—2.8 and 5.6 Mrads—were used for comparison, even though product temperature at irradiation was between ambient[15] and cryogenic.[16] Raw samples rather than cooked samples were analyzed, mainly to eliminate variables caused by the variety of heat treatments that might affect the results (Refs. 2, 3, 17, and 18).

Preparation of Test Samples

Skinless fillets were cut from 1-day-old fish purchased from a dealer in Gloucester, Mass., and were halved and packaged in heat-sealed polyethylene bags, with at least one nape section from one fillet and one tail section from another fillet in each bag. Cod and haddock were irradiated in the Marine Products Development Irradiator (MPDI) to a dose of 0.2 Mrad, given in 82 min. The irradiated samples were stored at 40°F (4.4°C) until evaluation. Doses of 2.8 and 5.6 Mrads were given to cod and haddock at the U. S. Army Natick Laboratories.

Analysis of Neutral *p*H Sample

Gas–liquid chromatographic analysis of volatile components has been used to characterize the chemical effects of radiation on seafoods. Mendelsohn et al.[19] showed that the number and quantity of volatile components detected are proportional to the radiation dose.

An exact amount of small fillet pieces was placed in a glass flask. Because neither acid nor alkali is added to this sample, it is called the neutral *p*H sample. The glassware and flask design are described by Merritt et al.[20] Use of this system in high vacuum distillation of fish samples is covered by Mendelsohn et al.[21] (The full details of sample preparation and gas-chromatographic conditions are given in the report from which this summary was prepared.)

The general effect of radiation was to increase the number and size of peaks in the chromatograms. These increases were clearly evident in the chromatograms of a control sample and the 0.2-Mrad sample (Fig. 1) for cod. Further increases are evident in the chromatograms of samples irradiated to higher doses; also, there is evidence that some of the volatile products of low-dose irradiation are fragmented again at higher doses into smaller, more volatile molecules. Along with results from previous studies,[9,19,22] these results demonstrate the desirability of reducing product temperature during irradiation, especially at sterilizing doses.

Likewise, the effect of storing samples at 40°F (4.4°C) was to increase the size and number of peaks on the chromatograms; these effects were generally additive to the radiation effects (Fig. 2).

Analysis of Alkaline *p*H Sample

Because radiation increases the number and quantity of neutral volatile components, other compounds such as basic polar compounds (e.g., amines) might also be produced or changed during irradiation. However, polar compounds in fresh ground fish muscle (*p*H ~6) might be insufficiently volatile to be detected. Accordingly the *p*H of the sample was adjusted to 12 by addition of 6*M* sodium hydroxide. Making the sample alkaline prevented the release of acidic and neutral components and limited the collection of volatile condensate to the basic components.

The number and concentrations of basic compounds detected tend to increase with increases in radiation dose and in duration of storage (Fig. 3), but the increases do not appear to be additive, although in specific components they may be. The differences between nonirradiated samples and samples irradiated at high doses are greater than differences between nonirradiated and low-dose irradiated samples. This result is expected since there is no evidence of organoleptic changes at the lower dose. In the samples irradiated at sterilizing doses, several compounds appeared that were either absent or present in very low concentrations in the nonirradiated or low-dose irradiated samples. These compounds may be useful as indicators of radiation treatment, but identification and quantification are necessary before conclusions can be made.

XUM

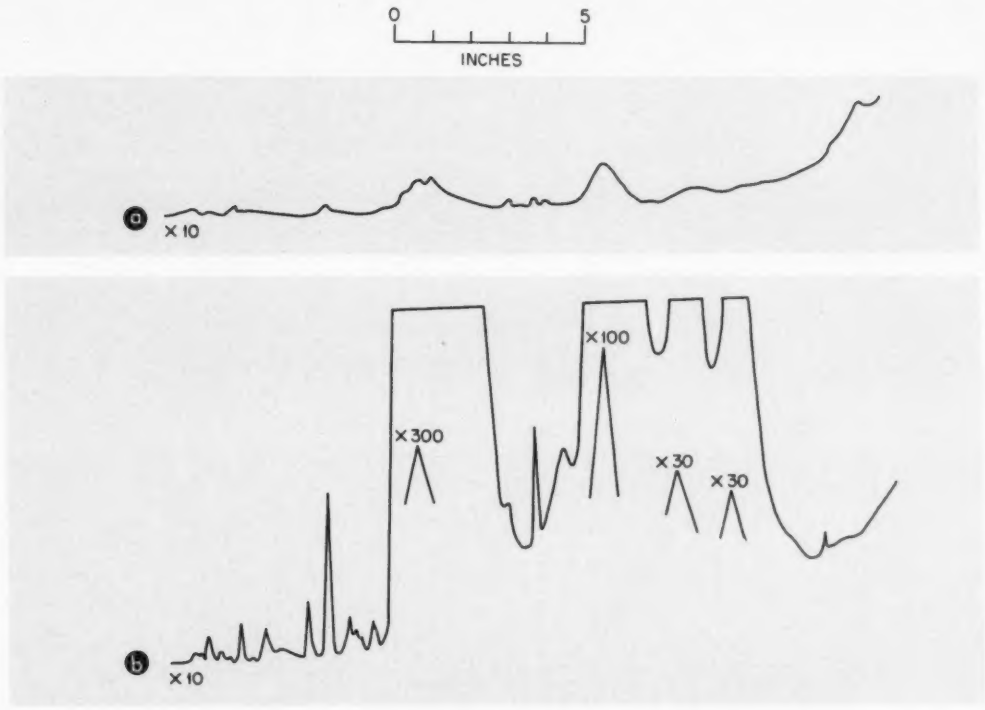


Fig. 1 Gas chromatogram of a headspace gas sample from (*a*) nonirradiated cod muscle and (*b*) 0.2-Mrad irradiated cod muscle.

Analysis of Water–Methanol Extract

The Bligh–Dyer technique[14] has been used to extract lipids from foodstuffs; also, it has the potential of extracting nonlipid components from tissue residue. Predetermined quantities of water, methanol, and chloroform are used to form two liquid phases and a tissue residue that is mostly denatured protein. Normally the chloroform phase is used to determine total lipids or certain classes of lipids, and the water–methanol phase is discarded with the tissue residue. However, the water–methanol phase probably contains several classes of nonlipid extractives, and the tissue residue might yield components to different or more drastic extraction methods. Accordingly the water–methanol phase was studied. The compounds responsible for the appearance of the gas chromatograms obtained from the fish samples are evidently soluble in the water–methanol phase of a Bligh–Dyer[14] extract, extractable from this phase into *n*-pentane, and less volatile than *n*-pentane itself. (The full report contains the details of preparation of water–methanol phase, *n*-pentane extraction, and microdistillation.)

Chromatograms from both cod and haddock showed peaks whose size increased with increase in dose in the range 0 to 2.8 Mrads; however, many peaks from the 5.6-Mrad sample were smaller than the corresponding peaks from the 2.8-Mrad sample (Fig. 4). Because highly volatile compounds were supposedly eliminated from the samples by the experimental methods used, the results support the hypothesis that some volatile products caused by low-dose radiation can be fragmented into smaller molecules by subsequent higher doses of radiation.

Effects of storage at 40°F (4.4°C) were similar for both species. Storage increased the number of peaks and seemed to reduce the size of some of the peaks (Fig. 5). Decreases in amounts of certain chemical components are to be expected since the system (i.e., fish fillets) is dynamic and maintains a continuing chemistry. Further experiments would be useful, provided they are based on the use of other extraction techniques and other chromatographic methods to determine the chemical effects of radiation on sugars, amino acids, nucleotides, and lipids in fish muscle.

XUM

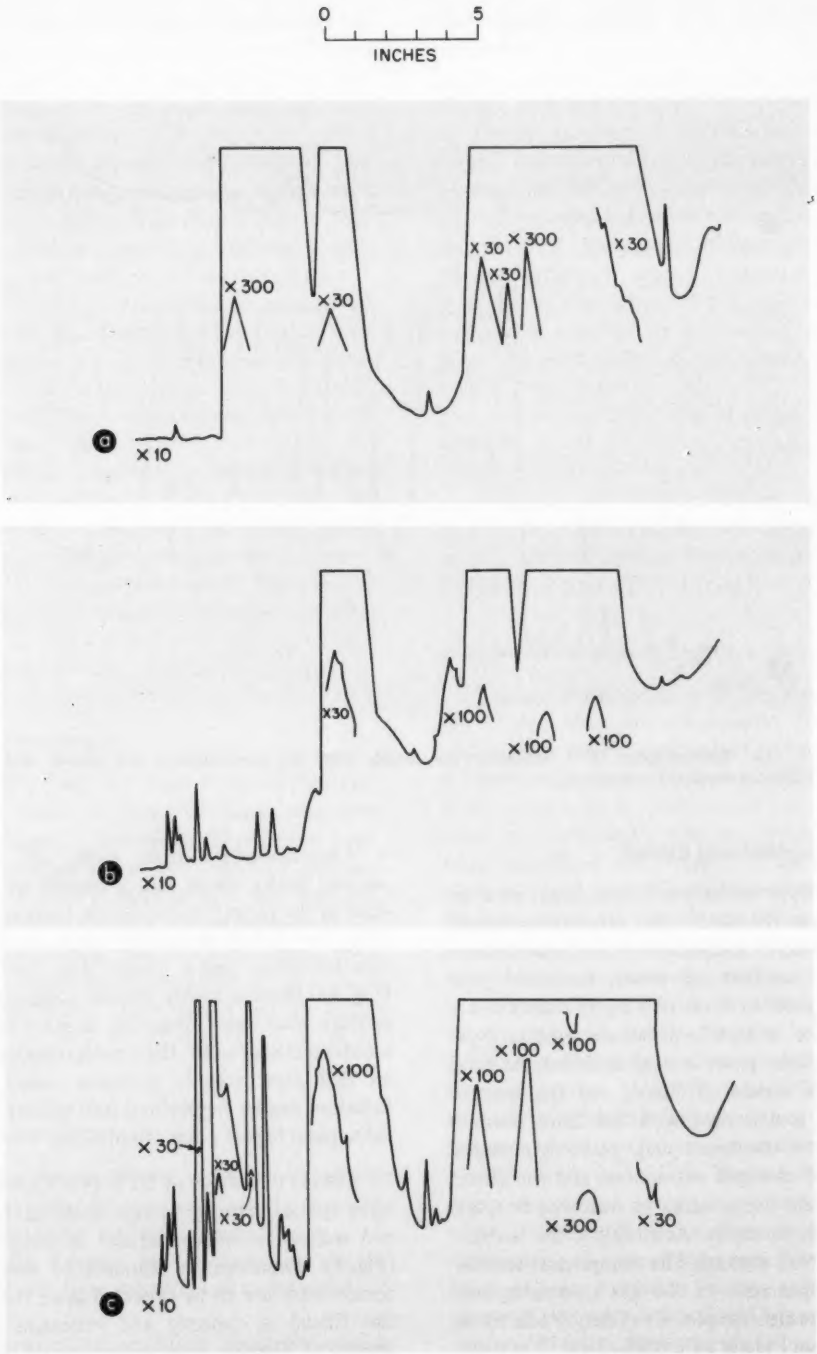


Fig. 2 Gas chromatogram of a headspace gas sample from (*a*) nonirradiated cod muscle stored 10 days at 40°F (4.4°C); (*b*) 0.2-Mrad irradiated cod muscle stored 10 days at 40°F (4.4°C); and (*c*) 0.2-Mrad irradiated cod muscle stored 29 days at 40°F (4.4°C).

XUM

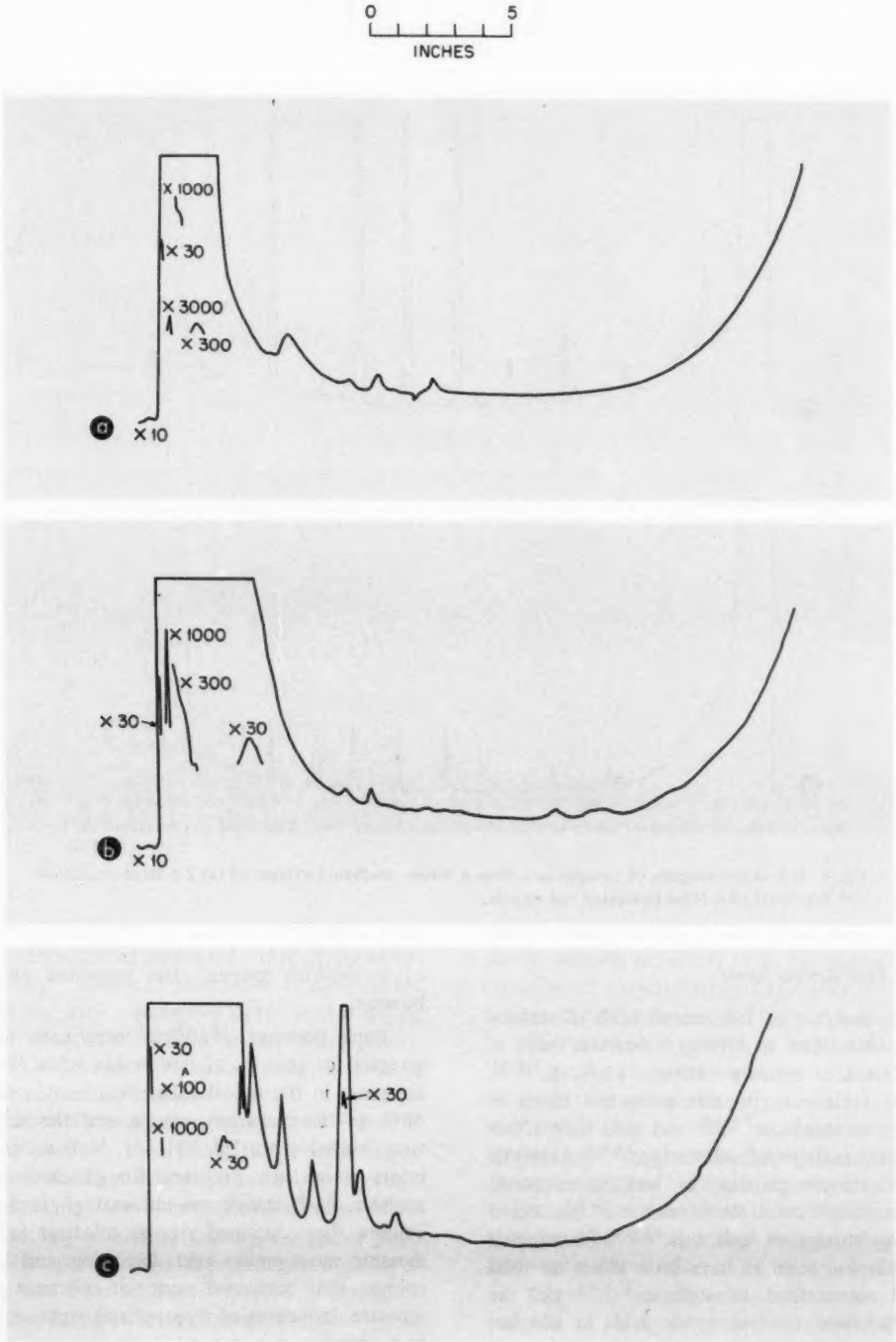


Fig. 3 Gas chromatogram of an alkaline headspace gas sample from (*a*) nonirradiated haddock muscle; (*b*) 0.2-Mrad irradiated haddock muscle stored 15 days at 40°F (4.4°C); and (*c*) 5.6-Mrad irradiated haddock muscle stored 32 days at 40°F (4.4°C).

XUM

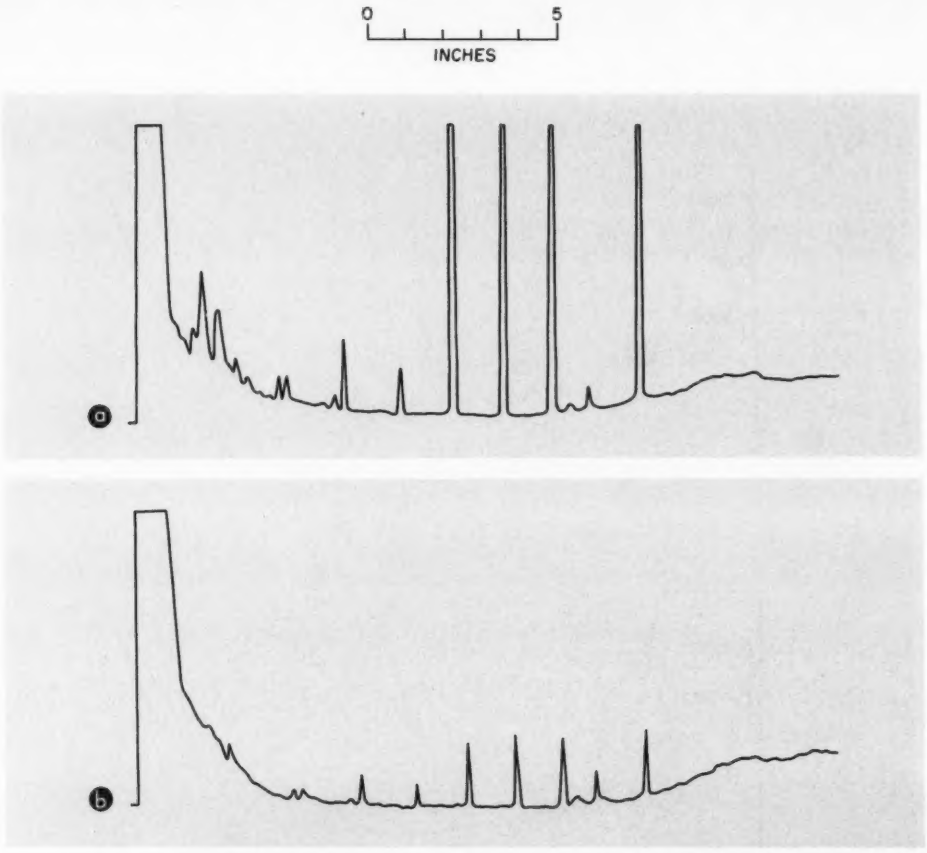


Fig. 4 Gas chromatogram of components from a water–methanol extract of (*a*) 2.8-Mrad irradiated cod muscle; (*b*) 5.6-Mrad irradiated cod muscle.

Analysis of Free Amino Acids

Previous analyses of free amino acids in seafood have been undertaken to develop a chemical index of quality in fresh or spoiling unfrozen seafoods.[23-35] Free amino acids may contribute to the flavor or acceptability of seafoods[36-38] and also may affect lipid oxidation during seafood storage.[39-41] Autolytic cleavage of muscle protein, as well as microbial activity, can contribute to the formation of free amino acids during storage of seafoods.[42-44] Pasteurizing doses of radiation seem to have little effect on total amino acid composition of seafoods,[2,3,45] but the effect of radiation on free amino acids in situ has received very little attention. Model-system studies[46,47] have shown that radiation can fragment amino acid molecules; therefore irradiation might be expected to decrease free amino acid content of seafood. Study of a shellfish species[2] has suggested an increase, however.

Nape portions of fillets were used to prepare samples for analysis of free amino acids. (Full details are given in the report.) The final extract was loaded onto an ion-exchange column, and the amino acids were eluted with 1*M* NH_4OH. Volatile amino acid esters were then prepared for gas-chromatographic analysis. Each sample was chromatographed first on a column that contained a polar substrate (adipate) to separate most amino acid derivatives and then on a column that contained nonpolar substrate (Ovid) to separate derivatives of tryptophane, arginine, histidine, and cystine.

The general effect of radiation was to increase the size or number of peaks. The effect was dose-dependent; the higher doses gave much larger increases

XUM

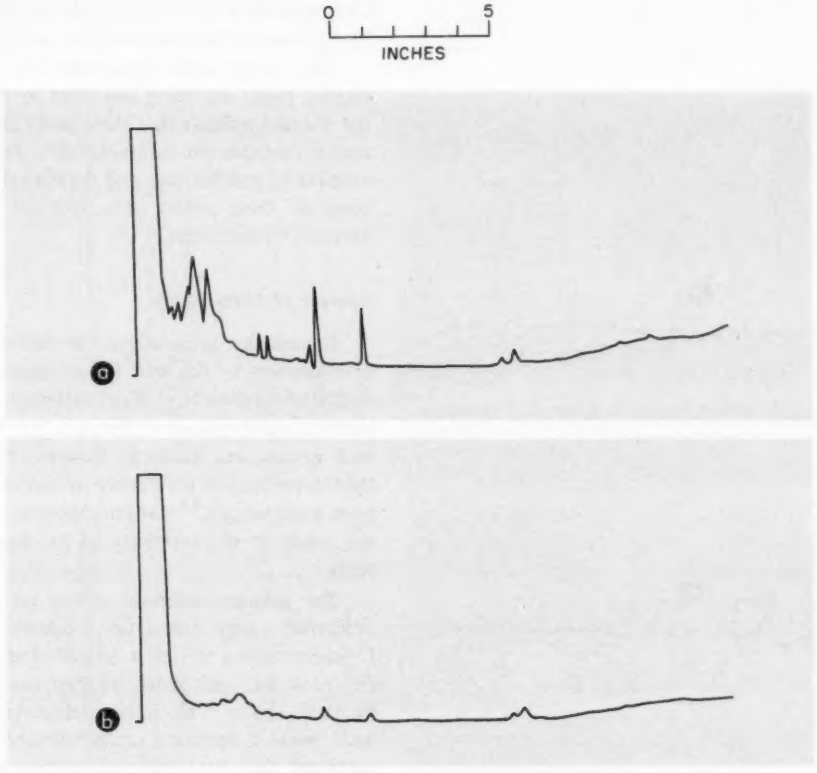


Fig. 5 Gas chromatogram of components from a water–methanol extract of (*a*) nonirradiated cod muscle stored 10 days at 40°F (4.4°C); (*b*) 0.2-Mrad irradiated cod muscle stored 29 days at 40°F (4.4°C).

in both size and number of peaks (Fig. 6), with some exceptions. This finding agrees with that of the earlier shellfish study.[2] Although destruction of some amino acid molecules may conceivably occur in situ during irradiation, results on all seafoods studied so far—clam,[2] cod, and haddock—indicate a net increase in free amino acid concentrations.

The effects of storing the samples at 40°F (4.4°C) can be explained by considering the relative importances of microbial spoilage and of enzymatic spoilage. In chromatograms from nonirradiated samples, where microbial activity is dominant, changes in size of peaks (Fig. 7) were much greater than changes in peaks of chromatograms from irradiated samples. In chromatograms of the 0.2-Mrad-treated samples, size of peaks increased during the first half of the storage period—enzymatic activity—and decreased during the second half of the storage period—microbial activity (Fig. 8). In chromatograms of 2.8- and 5.6-Mrad samples, there was a general increase in size of the peaks, presumably due to enzymatic activity (Fig. 9). Enzymatic activity (possibly of bacterial origin) evidently is the cause of storage effects in irradiated samples.

How irradiation causes an increase in free amino acids is not yet clearly understood. Three hypotheses invoked to explain this effect are: (1) Proteolytic enzymes in situ, perhaps of bacterial origin, may increase activity because of localized increases in thermal energy. (2) Peptide bands in situ may be broken by direct radiation hits. (3) Tissue structure may break down and thus increase the amount of extractable amino acid.

The radiation-induced increase in free amino acid content of seafoods may beneficially affect their nutritive value. Although seafoods are thought to be excellent sources of protein, their dietary value depends on the efficiency with which they are digested and utilized as well as on their amino acid composition.

XUM

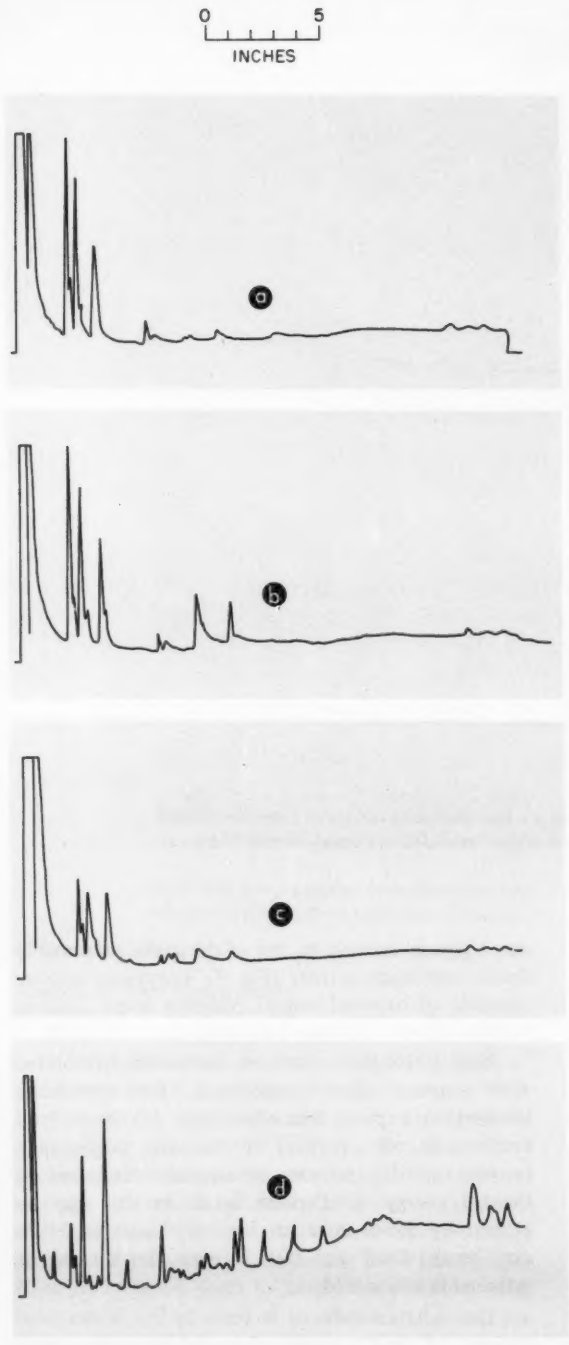


Fig. 6 Gas-chromatographic determination of free amino acids (Ovid column) from (*a*) nonirradiated cod muscle; (*b*) 0.2-Mrad irradiated cod muscle; (*c*) 2.8-Mrad irradiated cod muscle; (*d*) 5.6-Mrad irradiated cod muscle.

Consequently a nutritional study of protein utilization from irradiated seafood would be worthwhile.

The compounds responsible for the chromatographic peaks are being identified by mass spectrometry. Results indicate that these peaks are not caused by artifacts introduced unintentionally during the lengthy extraction, purification, and derivatization procedures. Some of these amino acids have not been identified previously in seafoods.

Analysis of Fatty Acids

Commercial preservation treatments can cause lipid deterioration in situ and reduce organoleptic acceptability of foodstuffs.[48] More attention so far has been given to fatty species of seafood than to lean species, such as cod and haddock; however, the influence of lipid deterioration on quality of cod and haddock has been documented.[49] Deterioration of seafood lipid is the result of the reactivity of its characteristic fatty acids.

The primary radiation effects on fatty acids are oxidative; many radiolytic products are formed.[50] Lipid-containing materials, including mackerel oil, beef fat, pork fat, and synthetic triglycerides, have been irradiated by a ^{60}Co source; their volatile products have been determined quantitatively.[51] Nawar has suggested that the type and relative amounts of the volatile products can be predicted if the nature of the irradiated lipid, the radiation dose, and the irradiation temperature are known.[51-55] These studies did not include synthetic phospholipids or lean species of fish, whose lipid content is 70 to 80% phospholipid.[49,56]

In this study, fatty acid composition of irradiated cod and haddock muscle has been determined. Lipids were extracted by the Bligh–Dyer procedure.[14] The total amount of lipids extracted was estimated to be 0.5 to 0.6 g per 100 g of cod flesh or 0.6 to 0.7 g per 100 g of haddock flesh. After further treatment, the extracts were analyzed by gas-liquid chromatography; polar, moderately polar, and nonpolar stationary liquid phases were used.

Methyl esters of fatty acids were identified by comparing chromatographic data with the data from Hormel Institute standards or from National Institutes of Health standard mixtures or by log plot and separation-factor procedures.[56-59] The relative amount of each ester present was determined by calculating the ratio of its peak area to the sum of all the peak areas. Results (Tables 5 to 8) are presented in tabular rather than chromatographic form because rapid identification procedures were used. Conven-

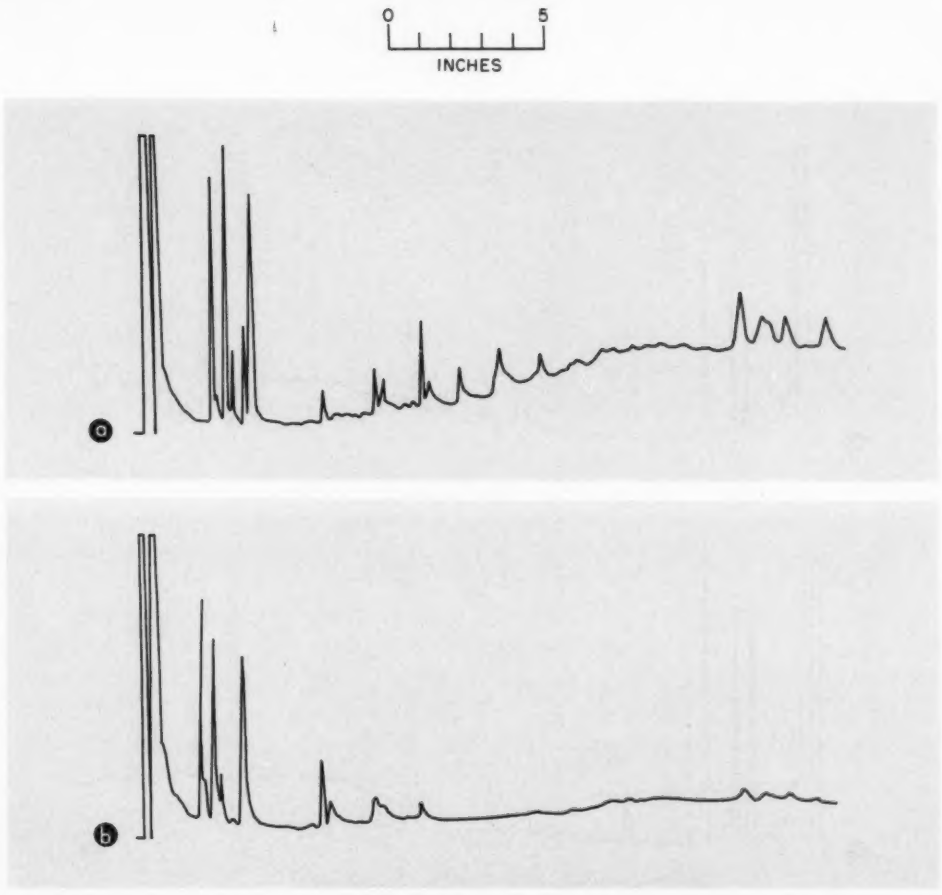


Fig. 7 Gas-chromatographic determination of free amino acids (Ovid column) from nonirradiated cod muscle stored (*a*) 10 days at 40°F (4.4°C); (*b*) 15 days at 40°F (4.4°C).

tional shorthand is used to describe the compounds (see footnote, Table 5), which are listed according to structural similarity.

Most of the compounds have been identified previously in nonirradiated cod or haddock muscle.[60-62] Compounds associated with peaks labeled RS20:4, RS20:5, and RS22:6 have not yet been identified. (These designations are used to indicate that the peaks were present only in the radiation-sterilized samples and that they appeared shortly after 20:4w6, 20:5w3, and 22:6w3, respectively.) The small peak 24X that appeared in some chromatograms may have been observed[60] previously, but the compound associated with it also remains unidentified. Some of the results are in general agreement with the hypothesis of Nawar[51] that radiation causes quantitative decreases in fatty acid concentrations. The appearance of three compounds was not predicted, probably because Nawar[51] measured volatile components obtained directly from irradiated samples.

Four of the fatty acids identified (16:0, 18:1w9, 20:5, and 22:6w3) are predominant components of cod and haddock lipid samples as well as representatives of their major classes of lipids.[60] Phospholipids, which are well dispersed in muscle tissues since they are included in membrane structures and are involved in the physiological functions of muscle tissue, are richer in polyenes (such as 20:5w3 and 22:6w3) and saturated fatty acids (such as 16:0) than are triglycerides. On the other hand, triglycerides are rich in monoenes (such as 18:1w9) and are not intimately dispersed in muscle tissue. Consequently a consider-

XUM

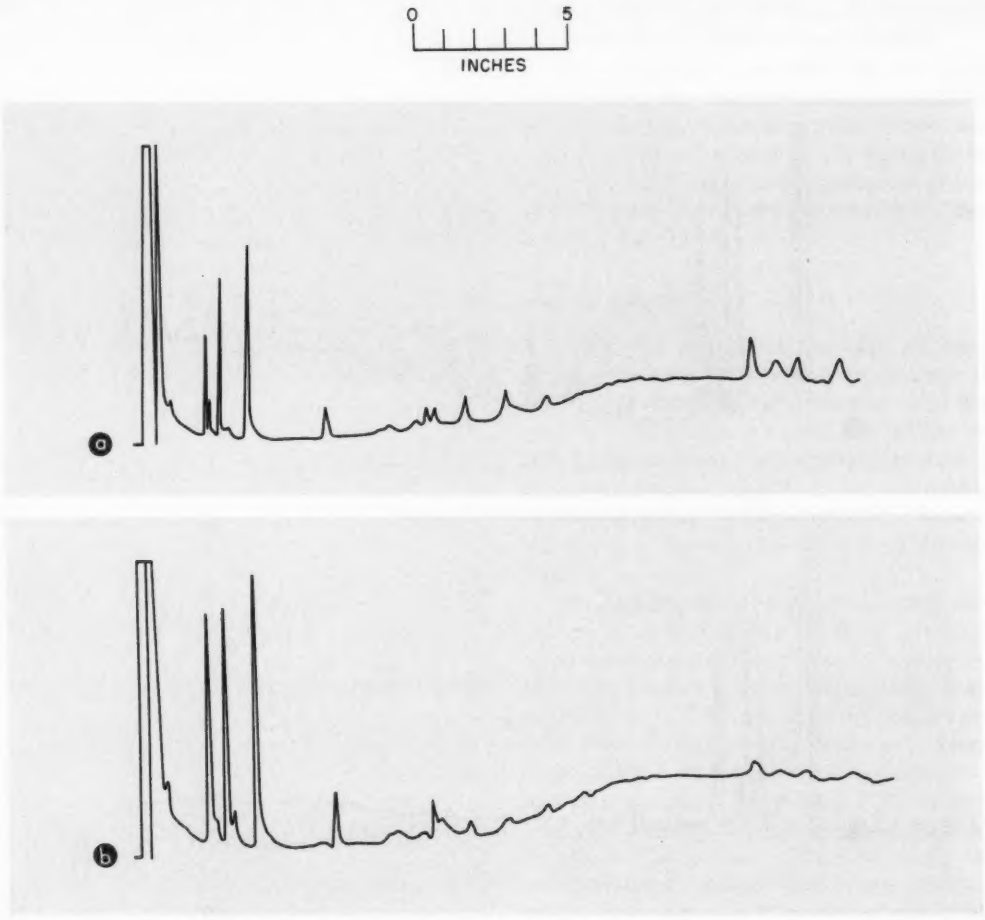


Fig. 8 Gas-chromatographic determination of free amino acids (Ovid column) from 0.2-Mrad irradiated cod muscle stored (*a*) 10 days at 40°F (4.4°C); (*b*) 29 days at 40°F (4.4°C).

ation of the location of a fatty acid molecule in situ and its chemical reactivity in vitro may aid in interpreting the results. For example, the decreases in 20:5w3 and 22:6w3 are not surprising, because these acids are concentrated in the lecithins, cephalins, and sterols and are highly reactive. Larger increases in the amount of 16:0 obtained from the irradiated sample might be expected because of its relative chemical inertness except that phospholipids contain about twice as much 16:0 as do nonphospholipids. Similarly, recovery of 18:1w9 is not unexpected in view of its high concentration in triglycerides and its chemical reactivity.

The interpretation of the effect of storage is based on the potential for microbial or autolytic enzymatic activity in the samples during storage. In general, storage seems to have little effect on fatty acid composition. Lipid hydrolysis is assumed to occur because lipids of nonirradiated fish muscle are known to deesterify during chilled storage; freezing treatments, which cause disorganization of muscle tissue, can accelerate this reaction.[61] The effect of radiation on the disorganization process in muscle tissue or on the rate of lipid hydrolysis has not been studied extensively, but there are indications that nonesterified fatty acids can be produced.[63] Present results indicate that, even if nonesterified fatty acids are formed during storage, they are not subsequently oxidized to any appreciable extent.

Nawar et al.[53] have suggested that the effect of radiation on lipids might become the basis for a test to

XUM

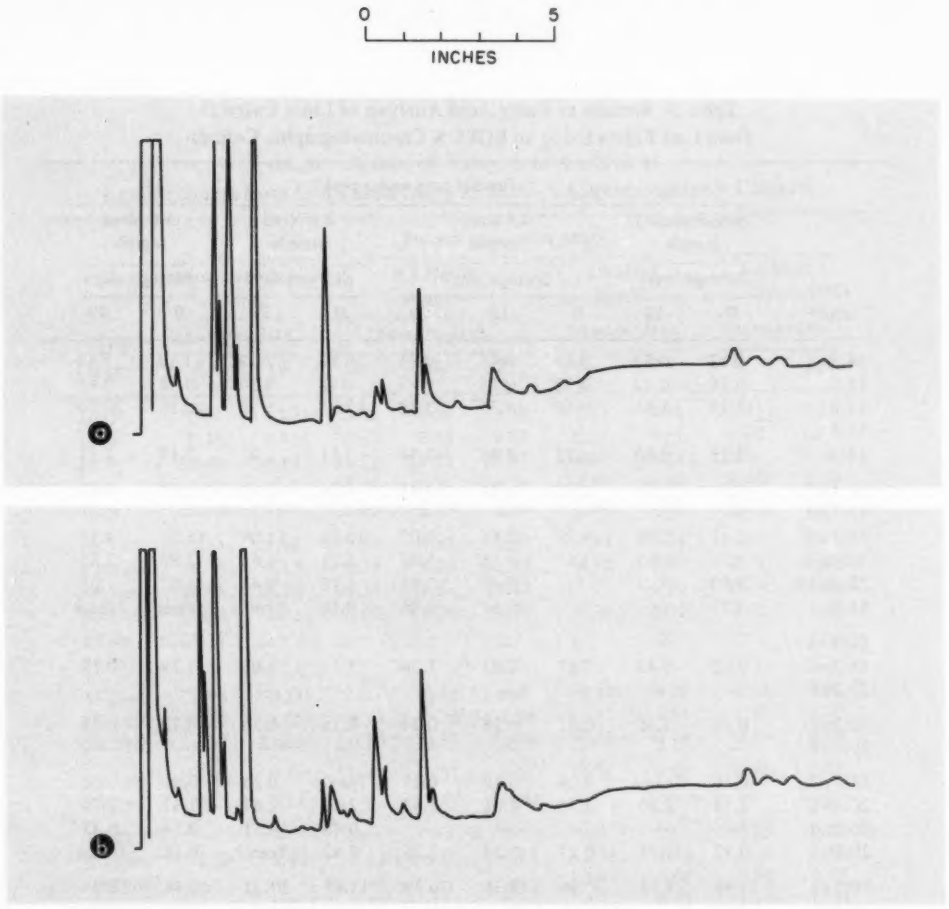


Fig. 9 Gas-chromatographic determination of free amino acid (Ovid column) from (*a*) 2.8-Mrad irradiated cod muscle stored 29 days at 40°F (4.4°C); (*b*) 5.6-Mrad irradiated cod muscle stored 29 days at 40°F (4.4°C).

determine whether or not seafood has been irradiated. Two obvious requirements are that the change caused by radiation be measurable and that the degree of this change be unaffected by storage of the seafood either before or after irradiation. Determination of polyunsaturated fatty acids or possibly the three new components might fulfill these requirements, but more study is needed to establish the reliability and practicality of any suggested method.

GENERAL DISCUSSION

Irradiated and nonirradiated cod and haddock fillets have been chemically analyzed for evidence of (1) the effect of radiation (using unstored samples), (2) the effect of storage (using samples given identical irradiation treatments), and (3) similarities or differences between the two species. The effect of radiation dose is shown by the fact that gas chromatograms of 0.2-Mrad-treated samples were more similar to chromatograms of untreated samples than to chromatograms of samples given 2.8 or 5.6 Mrads. The observed changes in the chromatograms were usually continuous with dose, except for some of the volatile components. The similarities between cod and haddock chromatograms far outweighed the differences, which is not surprising in view of the phylogenic and ecological similarities of these two species. This comparison is based on only one lot of each species, however, and seasonal variations between species can be expected.

Table 5 Results of Fatty Acid Analysis of Lipid Extracts from Cod Fillets Using an EGSS-X Chromatographic Column

Fatty acid*	Percent area under peak†								
	Nonirradiated sample		0.2-Mrad sample			2.8-Mrad sample		5.6-Mrad sample	
	Storage, days		Storage, days			Storage, days		Storage, days	
	0	10	0	10	29	0	29	0	29
14:0	0.52	0.80	0.63	0.48	0.91	0.97	1.29	1.12	0.73
15:0	0.26	0.12	0.33	0.25	0.53	0.32	0.54	0.42	0.43
16:0	15.28	14.84	9.50	14.30	13.80	17.63	16.79	10.76	20.70
17:0	—	—	—	—	—	—	—	—	—
18:0	3.19	2.80	3.75	4.88	3.44	3.51	2.97	7.58	4.33
16:1w7i	1.17	1.36	1.25	1.14	1.41	1.34	1.63	1.87	1.15
17:1w9	—	—	—	—	—	—	—	—	—
18:1w9	9.11	8.30	9.22	10.84	9.07	10.66	11.09	15.23	9.30
20:1w9i	1.73	1.68	1.61	1.15	1.96	2.21	1.63	3.80	2.53
22:1w11i	0.50	0.31		0.57	0.46	1.15	0.45	1.0	1.01
24:1i	0.19	—	—	0.37	0.88	0.16	Traces	Traces	Traces
16:2w4	—	—	—	—	—	—	—	—	—
18:2w6	0.82	0.43	0.67	0.83	1.06	1.11	1.09	1.79	0.79
20:2w6	—	—	—	—	—	—	—	—	—
18:3w6i	0.29	0.36	0.37	0.28	0.34	0.35	0.58	0.73	0.32
20:3w6	—	—	—	—	—	—	—	—	—
18:4w3	0.16	Traces	0.24	0.30	0.25	Traces	0.28	0.41	0.21
20:4w6	2.38	2.80	3.76	4.81	2.92	2.49	2.87	1.47	3.74
RS20:4	—	—	—	—	—	0.48	0.51	0.14	0.33
20:4w3	0.37	0.24	0.27	0.24	2.26	0.42	Traces	0.16	Traces
20:5w3	12.95	18.15	20.95	19.35	20.73	11.87	17.33	10.44	13.0
RS20:5	—	—	—	—	—	2.67	3.0	3.63	3.96
21:5w2	0.34	Traces	0.53	Traces	Traces	0.14	Traces	0.43	Traces
22:5w6	0.42	Traces	0.96	0.81	0.95	0.35	Traces	0.27	0.25
22:5w3	1.20	1.86	1.85	1.86	3.15	1.18	0.23	1.21	1.78
22:6w3	49.13	45.92	44.07	37.53	35.85	34.87	35.12	28.85	25.41
RS22:6	—	—	—	—	—	6.58	3.14	8.98	7.22
24X	—	—	—	—	—	Traces	—	—	—

*Determinations based on relative retention times and peak areas of methyl ester derivatives. Identifications are described in conventional shorthand. For example, 18:3w6i has 18 carbon atoms and 3 methylene interrupted double bonds; the terminal methyl group, w, is six carbon atoms from the ultimate double bond; and i signifies that other isomers of 18:3 (such as w3 or w9) may be present but not resolved chromatographically. The RS indicates that the compound occurred only in irradiated samples.

†A dashed line indicates no positive evidence for presence of this compound in the sample.

XUM

Table 6 Results of Fatty Acid Analysis of Lipid Extracts from Cod Fillets Using an EGSS-Y Chromatographic Column

	Percent area under peak†								
	Nonirradiated sample		0.2-Mrad sample			2.8-Mrad sample		5.6-Mrad sample	
	Storage, days		Storage, days			Storage, days		Storage, days	
Fatty acid*	0	10	0	10	29	0	29	0	29
14:0	0.96	1.27	1.05	0.84	1.35	1.81	2.04	1.73	1.10
15:0	0.48	0.43	0.40	0.45	0.83	0.54	0.94	0.60	0.47
16:0	29.46	26.10	26.22	29.25	25.92	34.0	29.24	30.0	29.68
17:0	0.37	0.51	0.38	0.35	2.94	0.44	0.34	0.40	1.39
18:0	5.60	5.49	6.03	7.45	5.96	5.96	4.89	6.85	6.44
16:1w7i	7.54	3.76	3.58	3.81	5.58	1.09	5.03	4.52	6.17
17:1w9	0.38	0.13	0.16	0.22	3.81	0.52	0.42	0.31	1.01
18:1w9	14.05	14.70	14.37	16.88	13.83	15.0	16.36	16.14	14.60
20:1w9i	2.56	2.73	2.05	1.26	1.70	2.20	1.53	2.31	2.39
22:1w	1.17	—	—	—	—	—	—	—	—
24:1i	—	—	—	—	—	—	—	—	—
16:2w4	0.95	0.13	—	0.11	3.0	0.32	0.28	0.20	0.94
18:2w6	1.55	1.08	1.36	1.29	2.98	1.77	1.51	1.56	1.20
20:2w6	0.12	Traces	0.10	0.17	Traces	0.16	0.18	0.13	0.09
18:3w6i	0.31	0.19	0.43	0.31	0.57	0.36	0.39	0.34	0.15
20:3w6	0.12	0.11	—	0.17	Traces	—	Traces	—	Traces
18:4w3	—	—	—	—	—	—	—	0.35	0.23
20:4w6	2.50	2.46	3.12	4.01	1.77	1.79	1.78	1.62	1.11
RS20:4	—	—	—	—	—	0.47	0.60	0.80	0.43
20:4w3	—	1.01	0.77	0.55	0.38	0.52	0.63	1.13	0.50
20:5w3	12.39	13.92	15.82	14.64	11.01	8.72	10.93	7.44	8.60
RS20:5	—	—	—	—	—	—	2.25	2.81	3.18
21:5w2	0.61	0.41	1.88	0.45	0.45	0.25	0.50	0.32	0.18
22:5w6	0.64	0.29	0.27	0.37	0.49	0.24	0.41	0.47	0.33
22:5w3	1.21	1.16	1.08	0.67	1.30	0.67	0.89	0.84	1.25
22:6w3	13.46	23.30	19.97	16.07	14.66	16.00	15.13	13.95	14.20
RS22:6	—	—	—	—	—	3.54	3.06	4.40	4.58
24X	1.87	—	0.52	0.52	1.03	0.84	0.78	0.90	0.54

*See the first footnote in Table 5.
†See the second footnote in Table 5.

Table 7 Results of Fatty Acid Analysis of Lipid Extracts from Haddock Fillets Using an EGSS-X Chromatographic Column

Fatty acid*	Percent area under peak†								
	Nonirradiated sample		0.2-Mrad sample			2.8-Mrad sample		5.6-Mrad sample	
	Storage, days		Storage, days			Storage, days		Storage, days	
	0	15	0	15	32	0	32	0	32
14:0	0.51	0.51	0.72	0.57	0.71	0.71	0.90	0.87	0.86
15:0	0.27	0.26	0.65	0.51	0.64	0.39	0.76	0.42	0.74
16:0	13.68	14.77	16.60	15.76	16.55	17.36	20.80	20.75	20.05
17:0	—	—	—	—	—	—	—	—	—
18:0	3.95	3.94	3.65	3.82	3.64	4.50	4.43	4.58	4.63
16:1w7i	0.87	1.32	1.00	1.23	1.43	0.97	1.13	1.50	1.69
17:1w9	—	—	—	—	—	—	—	—	—
18:1w9	8.48	8.61	10.04	9.66	9.42	9.76	11.46	12.66	12.13
20:1w9i	1.23	1.19	2.23	1.82	2.53	2.02	2.00	2.86	1.19
22:1w11i	0.40	0.51	0.64	0.86	0.37	0.10	0.86	1.09	0.83
24:1i	0.77	—	—	0.96	1.0	0.33	0.33	0.26	0.78
16:2w4	—	—	—	—	—	—	—	—	—
18:2w6	0.66	0.66	0.57	0.61	0.62	1.07	1.14	1.08	1.64
20:2w6	—	—	—	—	—	—	—	—	—
18:3w6i	0.35	0.12	0.47	0.38	0.39	0.50	0.24	0.59	0.30
20:3w6	—	—	—	—	—	—	—	—	—
18:4w3	0.24	0.11	0.50	0.67	0.28	0.40	0.13	0.63	0.17
20:4w6	3.68	4.25	2.66	4.20	5.57	2.89	2.68	2.24	3.40
RS20:4	—	—	—	—	—	0.40	0.19	0.62	0.92
20:4w3	0.62	0.42	0.79	0.42	0.35	0.85	0.10	0.50	0.26
20:5w3	20.41	20.53	20.94	23.07	30.21	16.41	16.87	12.18	15.18
RS20:5	—	—	—	—	—	3.07	2.29	3.78	5.57
21:5w2	0.36	0.57	—	0.30	0.29	0.29	0.10	0.09	0.14
22:5w6	1.06	1.06	0.78	0.73	0.74	0.72	0.18	0.29	0.43
22:5w3	2.70	2.63	1.59	1.75	3.45	2.06	2.10	1.01	1.45
22:6w3	39.75	37.90	35.51	32.62	21.80	30.89	24.48	26.01	21.33
RS22:6	—	—	—	—	—	4.29	5.22	5.98	6.31
24X	—	—	—	—	—	—	—	—	—

*See the first footnote in Table 5.
†See the second footnote in Table 5.

Table 8 Results of Fatty Acid Analysis of Lipid Extracts from Haddock Fillets Using an EGSS-Y Chromatographic Column

Fatty acid*	Percent area under peak†								
	Nonirradiated sample		0.2-Mrad sample			2.8-Mrad sample		5.6-Mrad sample	
	Storage, days		Storage, days			Storage, days		Storage, days	
	0	15	0	15	32	0	32	0	32
14:0	1.36	0.90	1.01	1.06	1.06	1.10	1.21	1.56	1.10
15:0	0.53	0.47	0.44	0.45	0.83	0.47	0.37	0.63	1.01
16:0	29.30	28.78	44.94	31.75	31.01	35.76	34.33	31.28	31.98
17:0	1.27	1.43	1.36	1.49	0.95	1.02	0.91	1.15	0.97
18:0	9.48	5.44	5.45	4.83	5.23	6.75	6.27	6.58	5.18
16:1w7i	3.03	10.0	3.55	5.18	5.66	4.77	4.35	6.02	5.47
17:1w9	0.94	0.79	1.58	1.16	1.12	1.05	0.78	0.74	1.45
18:1w9	13.59	11.76	12.36	16.98	14.29	13.19	14.59	17.01	15.66
20:1w9i	1.08	1.04	1.74	1.53	0.69	1.57	1.53	2.50	0.89
22:1w11i	—	—	—	—	—	—	—	—	—
24:1i	—	—	—	—	—	—	—	—	—
16:2w4	0.78	0.75	1.13	0.86	0.60	1.00	0.55	0.68	0.81
18:2w6	1.68	1.04	2.08	1.44	1.19	1.21	1.50	1.67	1.95
20:2w6	0.14	0.11	0.24	0.11	0.09	0.17	0.16	0.23	0.06
18:3w6i	0.31	0.32	1.01	0.26	0.32	0.33	0.30	0.10	0.30
20:3w6	0.04	—	—	0.08	0.06	0.09	0.07	0.10	0.07
18:4w3	0.65	0.24	1.01	0.27	0.57	0.30	0.29	0.41	0.25
20:4w6	2.58	2.75	1.54	2.54	4.09	1.58	1.63	1.41	1.88
RS20:4	—	—	—	—	—	0.39	0.44	0.52	0.85
20:4w3	0.21	0.19	0.28	0.27	0.29	0.35	0.34	0.58	0.55
20:5w3	13.15	13.40	8.72	13.45	18.60	10.28	9.04	7.39	9.13
RS20:5	—	—	—	—	—	3.09	2.70	2.70	4.18
21:5w2	0.65	0.52	0.34	0.27	0.51	0.22	0.27	0.23	0.38
22:5w6	0.33	0.34	0.38	0.24	0.28	0.21	0.20	0.25	0.21
22:5w3	1.14	1.18	0.41	1.02	1.50	0.67	0.75	0.75	0.72
22:6w3	16.11	17.95	10.48	14.43	10.14	11.84	14.07	11.22	10.18
RS22:6	—	—	—	—	—	2.09	2.80	3.53	4.25
24X	1.09	0.58	0.54	0.33	0.32	0.50	0.55	0.49	0.57

*See the first footnote in Table 5.
†See the second footnote in Table 5.

XUM

The various effects of storage have been explained in terms of microbial or enzymatic spoilage; consideration of these results indicates that an after-the-fact irradiation test is possible but needs more work.

The available evidence suggests that further study is needed of the effects of radiation on tissue structure or function. The observed decreases in polyunsaturated fatty acids and increases in free amino acids support the hypothesis[64-67] that radiation alters the structure of cellular membranes. Conceivably, a simple colorimetric test based on altered membrane permeability could be developed to determine whether or not seafood has been irradiated.

The gas-chromatographic results support the original rationale that radiation fragments a wide variety of chemical compounds in situ into several types of smaller molecules. Further work to determine which volatile components are most responsive to radiation might lead to another test to tell whether or not seafood has been irradiated. The chemical pyrolysis test of MacGee[68] warrants study because it is sensitive, reliable, and simple. Some of these proposals for future study may be undertaken with Bureau of Commercial Fisheries support. The Bureau is already supporting work to identify components by mass spectrometry; the results will be published separately. (FEM)

REFERENCES

References marked with an asterisk have not been verified by the editors; for further explanation, see the Foreword.

1. J. W. Slavin, L. J. Ronsivalli, J. D. Kaylor, and J. H. Carver, Study of Irradiated-Pasteurized Fishery Products, USAEC Report TID-22833, Bureau of Commercial Fisheries, 1965.
2. R. O. Brooke, E. M. Ravesi, D. F. Gadbois, and M. A. Steinberg, Preservation of Fresh Unfrozen Fishery Products by Low-Level Radiation. 3. The Effects of Radiation-Pasteurization on Amino Acids and Vitamins in Clams, *Food Technol.*, **18**(7): 116-120 (1964).
3. R. O. Brooke, E. M. Ravesi, D. F. Gadbois, and M. A. Steinberg, Preservation of Fresh Unfrozen Fishery Products by Low-Level Radiation. 5. The Effects of Radiation-Pasteurization on Amino Acids and Vitamins in Haddock Fillets, *Food Technol.*, **20**(11): 99-102 (1966).
4. L. J. Ronsivalli, J. B. Bernstein, and B. L. Tinker, Method for Determining the Bacterial Permeability of Plastic Films, *Food Technol.*, **20**(8): 98-99 (1966).
5. J. W. Slavin and L. J. Ronsivalli, Study of Irradiated-Pasteurized Fishery Products, USAEC Report TID-19969, Bureau of Commercial Fisheries, 1963.
6. T. J. Sinskey, I. S. Pablo, G. J. Silverman, and L. J. Ronsivalli, The Effect of Packaging on the Major Microbial Flora of Irradiated Haddock, *Nature*, **213**(5074): 425-426 (Jan. 28, 1967).
7. J. J. Licciardello, L. J. Ronsivalli, and J. W. Slavin, Effect of Oxygen Tension on the Spoilage Microflora of Irradiated and Nonirradiated Haddock Fillets, *J. Appl. Bacteriol.*, **30**(1): 239-245 (1967).
*8. P. G. Scheurer, Penetration Gradients of Sodium Nitrite and Sodium Tripolyphosphate in Haddock Fillets, *J. Food Sci.*, **33**(5): 504-506 (1968).
9. L. J. Ronsivalli, V. G. Ampola, F. J. King, and J. A. Holston, Study of Irradiated-Pasteurized Fishery Products, USAEC Report TID-24256, Bureau of Commercial Fisheries, 1967.
10. S. A. Goldblith and J. T. R. Nickerson, The Effect of Gamma Rays on Haddock and Clams Inoculated with *Clostridium botulinum* Type E, Annual Report, Oct. 1, 1964–Sept. 30, 1965, USAEC Report MIT-3325-B21, Massachusetts Institute of Technology, 1965.
11. Status of the Food Irradiation Program, Hearings Before the Subcommittee on Research, Development, and Radiation of the Joint Committee on Atomic Energy, Congress of the United States, 90th Congress, 2nd Session, July 18 and 30, 1968.
12. M. R. Burton, Radiation Chemistry, *Chem. Eng. News*, 47(6): 86-96 (Feb. 10, 1969).
13. M. Fujimaki and M. Morita, Radiation Chemistry of Foods. Part 1. Reaction Rate Constants of Some Food Constituents with Hydrated Electrons and Hydroxyl Radicals, *Agr. Biol. Chem.*, **32**(5): 574-579 (1968).
*14. E. G. Bligh and W. J. Dyer, A Rapid Method of Total Lipid Extraction and Purification, *Can. J. Biochem. Physiol.*, **37**: 911-917 (1959).
15. E. F. Reber, K. Raheja, and D. Davis, Wholesomeness of Irradiated Foods. An Annotated Bibliography, *Fed. Proc.*, **25**(5) Part I: 1530-1579 (1966).
16. E. S. Josephson, A. Brynjolfsson, and E. Wierbicki, Engineering and Economics of Food Irradiation, *Trans. N. Y. Acad. Sci.*, Series II, **30**(4): 600-614 (1968).
17. D. F. Gadbois, J. M. Mendelsohn, and L. J. Ronsivalli, Effects of Radiation, Heating, and Storage on Volatile Carbonyl Compounds in Clam Meats, *J. Food Sci.*, **32**(5): 511-515 (1967).
18. J. M. Mendelsohn and R. O. Brooke, Radiation, Processing, and Storage Effects on the Head-Gas Components in Clam Meats, *Food Technol.*, **22**(9): 1162-1166 (1968).
*19. J. M. Mendelsohn, F. J. King, and D. F. Gadbois, Effect of Irradiation Dose Level on the Headspace Gas Components Obtained from Haddock, in Proceedings of the 29th Annual Meeting, Institute of Food Technologists, pp. 104-105, May 11–16, 1969.
20. C. Merritt, Jr., S. R. Bresnick, M. L. Bazinet, J. T. Walsh, and P. Angelini, Determination of Volatile Components in Foodstuffs. Techniques and Their Application to Studies of Irradiated Beef, *J. Agr. Food Chem.*, **7**: 784-787 (1959).
*21. J. M. Mendelsohn, M. A. Steinberg, and C. Merritt, Jr., Techniques for Collecting Volatile Components from Haddock Flesh for Gas Chromatographic Analysis, *J. Food Sci.*, **31**(3): 389-394 (1966).
22. R. O. Brooke, Bureau of Commercial Fisheries, Gloucester, Mass., unpublished.
*23. F. A. L. Bramstedt, Amino Acid Composition of Fresh Fish and Influence of Storage and Processing, in *Fish in Nutrition*, pp. 61-67, E. Heen and R. Kreuzer (Eds.), Fishing News (Books) Ltd., London, 1962.

XUM

24. N. Dambergs, P. Odense, and R. Guilbault, Changes in Free Amino Acids in Skeletal Muscle of Cod (*Gadus morhua*) Under Conditions Simulating Gill Net Fishing, *J. Fish. Res. Board Can.*, **25**(5): 935-942 (1968).

*25. M. S. Hujita, S. Yeh, and S. Ikeda, Studies on Chemical Components of Japanese Pearl-Oyster Meat. I. Constituents of the Extracts of Adductor Muscles, *Bull. Jap. Soc. Sci. Fish.*, **34**(2): 146-149 (1968).

*26. N. R. Jones, The Free Amino Acids of Fish. I. Taurine in the Skeletal Muscles of Codling (*Gadus callarias*), *J. Sci. Food Agr.*, **6**(1): 3-9 (1955).

*27. N. R. Jones, The Free Amino Acids of Fish. 1-Methylhistidine and Beta-alanine Liberation by Skeletal Muscle Anserinase of Codling (*Gadus callarias*), *Biochem. J.*, **60**: 81-87 (1955).

*28. N. R. Jones, The Free Amino Acids of Fish. II. Fresh Skeletal Muscle from Lemon Sole (*Pleuronectes microcephalus*), *J. Sci. Food Agr.*, **10**(5): 282-286 (1959).

*29. H. Schaefer, Free Amino Acids and Their Relationship in Body Muscle of Fresh Caught Marine Bony Fish (in German), *Helgolaender Wiss. Meeresuntersuch.*, **8**(2): 257-275 (1962).

*30. H. Schaefer, Free Amino Acids and Their Relationship in the Musculature of Chimera and Some Elasmobranches and Invertebrates (in German), *Helgolaender Wiss. Meeresuntersuch.*, **8**(2): 280-286 (1962).

*31. H. Schaefer, Investigation of Post-mortem Changes of Stable Low-Molecular Nitrogen Compounds in Muscles of Seafish (in German), *Helgolaender Wiss. Meeresuntersuch.*, **8**(4): 383-403 (1963).

*32. J. M. Shewan, L. I. Fletcher, S. M. Partridge, and R. C. Brimley, Nitrogenous Extractives from Fresh Haddock Muscle: Fractionation with Ion-Exchange Resins, *J. Sci. Food Agr.*, **3**(9): 394-398 (1952).

*33. J. M. Shewan, The Nitrogenous Extractives from Fresh Fish Muscle. II. Comparison of Several Gadoid and Elasmobranch Species, *J. Sci. Food Agr.*, **4**(12): 565-568 (1953).

*34. J. M. Shewan, The Nitrogenous Extractives from Fresh Fish Muscle. III. Comparison of Several Flat Fishes and Members of the Herring-Mackerel Group, *J. Sci. Food Agr.*, **6**(2): 99-104 (1955).

*35. J. M. Shewan and N. R. Jones, Chemical Changes Occurring in Cod Muscle During Chill Storage and Their Possible Use as Objective Indices of Quality, *J. Sci. Food Agr.*, **8**(8): 491-498 (1957).

*36. Y. Hashimoto, Taste-producing Substances in Marine Products, in *The Technology of Fish Utilization*, pp. 57-60, R. Kreuzer (Ed.), Fishing News (Books) Ltd., London, 1965.

*37. A. Kawai, M. Sakaguchi, and M. Kimata, Histidine Metabolism in Fish. I. Histidine Deaminase and Urocanase Activities in Fish Muscle and Liver, *Mem. Res. Inst. Food Sci., Kyoto Univ.*, **28**: 18-25 (1967).

*38. A. Lukton and H. S. Olcott, Content of Free Imidazole Compounds in the Muscle Tissue of Aquatic Animals, *Food Res.*, **23**(6): 611-618 (1958).

*39. R. Marcuse, Effect of Amino Acids on Fat Oxidation. I. Investigation with Herring Oil (in German), *Ernaehrungsindustrie*, **63**(6): 547-549 (1961).

*40. R. Marcuse, The Effect of Some Amino Acids on the Oxidation of Linoleic Acid and Its Methyl Ester, *J. Amer. Oil Chem. Soc.*, **39**(2): 97-103 (1962).

*41. S. Matsushita and N. Iwami, Re-examination on the Antioxidative Effects of Amino Acids and Nucleic Acid Bases on the Oxidation of Unsaturated Fatty Acids, *Bull. Res. Inst. Food Sci., Kyoto Univ.*, **30**: 1-4 (1967).

*42. G. Siebert and A. Schmitt, Fish Tissue Enzymes and Their Role in the Deteriorative Changes in Fish, in *The Technology of Fish Utilization*, pp. 47-52, R. Kreuzer (Ed.), Fishing News (Books) Ltd., London, 1965.

*43. G. Siebert, A. Schmitt, and I. Bottke, Enzymes of Amino Acid Metabolism in Codfish Muscle (in German), *Arch. Fischereiwiss.*, **15**(3): 233-244 (1965).

*44. A. Schmitt, G. Siebert, and I. Bottke, Comparative Investigation of Dipeptidase Activity in Fish Tissue (in German), *Arch. Fischereiwiss.*, **17**(1): 50-60 (1966).

*45. K. Shirai and T. Oku, Determination of Amino Acids in Gamma-Irradiated Tuna Extract, *Bull. College Agr. Vet. Med., Nihon Univ.*, **26**: 1-8 (1968).

46. W. M. Garrison, Radiation Chemistry of Organo-nitrogen Compounds, in *Current Topics in Radiation Research*, Vol. 4, pp. 43-94, M. Ebert and A. Howard (Eds.), John Wiley & Sons, Inc., New York, 1968.

47. W. A. Armstrong and W. G. Humphreys, Amino Acid Radicals Produced Chemically in Aqueous Solutions. Electron Spin Resonance Spectra and Relation to Radiolysis Products, *Can. J. Chem.*, **45**(21): 2589-2597 (1967).

*48. H. W. Schultz, E. A. Day, and R. O. Sinnhuber (Eds.), *Symposium on Foods: Lipids and Their Oxidation*, Avi Publishing Co., Westport, Conn., 1962.

*49. R. G. Ackman, The Influence of Lipids on Fish Quality, *J. Food Technol.*, **2**: 169-181 (1967).

*50. J. R. Chipault, High Energy Irradiation, in *Symposium on Foods: Lipids and Their Oxidation*, pp. 151-169, H. W. Schultz, E. A. Day, and R. O. Sinnhuber (Eds.), Avi Publishing Co., Westport, Conn., 1962.

51. W. W. Nawar, Stability of Food Lipids to Ionizing Radiation, USAEC Report NYO-3499-3, Massachusetts University, Department of Food and Science Technology, February 1968.

52. W. W. Nawar, Stability of Food Lipids to Ionizing Radiation, in Seventh Annual AEC Food Irradiation Contractors' Meeting, USAEC Report CONF-670945, pp. 174-177, 1967.

*53. W. W. Nawar, J. C. Champagne, and M. F. Dubravcic, Approach to the Development of a Radiation Test for Foods, in Proceedings of the 28th Annual Meeting, Institute of Food Technologists, p. 133, 1968.

*54. W. W. Nawar, J. R. Champagne, M. F. Dubravcic, and P. R, Letellier, Recovery and Measurement of the Volatiles Formed in Lipid Systems by Irradiation, Proceedings of the 156th National Meeting, American Chemical Society, 1968.

*55. W. W. Nawar, M. R. Dubravcic, J. R. Champagne, J. P. Kavalam, and P. R. Letellier, Effects of High Energy Radiation on Lipids, Proceedings of the 42nd Meeting, American Oil Chemists Society, pp. 50-51, 1968.

*56. R. G. Ackman, Structural Correlation of Unsaturated Fatty Acid Esters Through Graphical Comparison of Gas-Liquid Chromatographic Retention Times on a Polyester Substrate, *J. Amer. Oil Chem. Soc.*, **40**(10): 558-564 (1963).

57. R. G. Ackman and R. D. Burgher, A Proposed Basis for the Systematic Identification of Unsaturated Fatty Acid Esters

XUM

Through Gas-Liquid Chromatography on Polyester Substrates, *J. Chromatogr.*, **11**: 185-194 (1963).

*58. R. G. Ackman and R. D. Burgher, Cod Liver Oil Fatty Acids as Secondary Reference Standards in the GLC of Polyunsaturated Fatty Acids of Animal Origin: Analysis of a Dermal Oil of the Atlantic Leatherback Turtle, *J. Amer. Oil Chem. Soc.*, **42**(1): 38-42 (1965).

59. R. G. Ackman, J. C. Sipos, and P. M. Jangaard, A Quantitation Problem in the Open Tubular Gas Chromatography of Fatty Acid Esters from Cod Liver Lipids, *Lipids*, **2**(3): 251-257 (1967).

60. R. F. Addison, R. G. Ackman, and J. Hingley, Distribution of Fatty Acids in Cod Flesh Lipids, *J. Fish. Res. Board Can.*, **25**(10): 2083-2090 (1968).

*61. J. Olley and W. R. H. Duncan, Lipids and Protein Denaturation in Fish Muscle, *J. Sci. Food Agr.*, **16**(2): 99-104 (1965).

*62. E. H. Gruger, Jr., Fatty Acid Composition of Fish Oils, in *Fish Oils*, pp. 3-30, M. E. Stansby (Ed.), Avi Publishing Co., Westport, Conn., 1967.

63. R. G. Ackman, J. E. Stewart, and H. E. Power, Free Fatty Acid Formation in Cod Livers Sterilized by Irradiation, *J. Fish. Res. Board Can.*, **23**(1): 155-156 (1966).

64. R. O. Sinnhuber and J. S. Lee, Effect of Irradiation on the Microbial Flora Surviving Irradiation Pasteurization of Seafoods, Final Summary, May 1963–April 1964, USAEC Report SAN-100-1, 1964.

65. B. O. Stuart and J. N. Stannard, The Radioprotection of *Saccharomyces cerevisiae* by Cystamine as Measured by Different Criteria of Cell Damage, *Radiat. Res.*, **28**(3): 609-623 (1966).

66. R. M. Sutherland, J. N. Stannard, and R. I. Weed, Involvement of Sulphhydryl Groups in Radiation Damage to the Human Erythrocyte Membrane, *Int. J. Radiat. Biol.*, **12**(6): 551-564 (1967).

67. A. M. Sutton and D. Rosen, Effect of X-Rays on the Electrical Conductance of Phospholipid Bilayer Membranes, *Nature*, **219**(5150): 153-154 (July 13, 1968).

68. J. MacGee, Characterization of Mammalian Tissues and Microorganisms by Gas-Liquid Chromatography, *J. Gas Chromatogr.*, **6**(1): 48-52 (1968).

XUM

Section
IV
Isotopes and Radiation Technology

Isotopic Heat and Power Development

ORNL Isotope Kilowatt Program

By A. P. Fraas*

Supplementary Keywords: *energy source; conversion, electric; conversion, kinetic; dynamic system; thermoelectric system.*

In April 1967 a conference[1] in Washington, D. C., on energy sources included discussions on radioisotopic power sources. The energy output of sources then available was less than 0.1 kW, although higher power sources were even then under development.

In 1968 Oak Ridge National Laboratory (ORNL) started work on a program† to evaluate various types of radioisotopic energy conversion systems for the production of 1 to 10 kW of electric power for terrestrial and undersea applications. The first phase of the program—a parametric and engineering analysis comparing the principal isotopic fuels and the principal types of energy-conversion systems plus preparation of conceptual designs for the more attractive systems—was completed[2] in the summer of 1969.

In October 1969 ORNL was asked to proceed with a detailed engineering study of the three most promising systems developed in Phase I, i.e., a 5-kW(e) organic Rankine-cycle system, a 3-kW(e) steam Rankine-cycle system, and a 2-kW(e) thermoelectric system. A program for a 3-year effort for calendar years 1970–1972 was planned, following reexamination of the conceptual designs presented in the Phase I report and consideration of possible improvements. The objective is to evolve by December 1972 a set of designs for two prototype power plants with a clear delineation of the development required in each case, including the cost and time for the various program steps. Because of limited funds and the desirability of narrowing the field to a single Rankine-cycle system, particular attention was given to the relative merits of the organic and steam Rankine-cycle systems.

ORGANIC RANKINE-CYCLE SYSTEM

The Rankine-cycle system under study (Fig. 1), except for the regenerator, is a conventional system with the turbine, generator, and boiler feed pump on a single shaft. The regenerator increases the system efficiency by recovering the enthalpy difference between the superheated and saturated vapors.

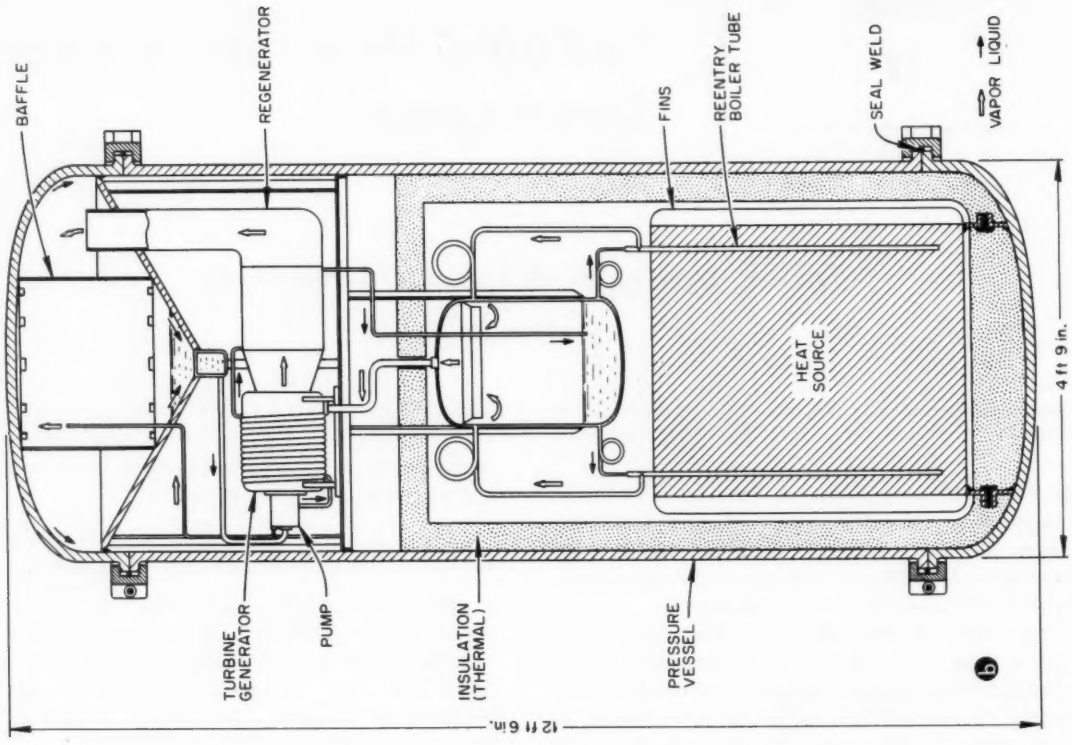
Review of available information on organic working fluids indicated that Dowtherm A was the only organic fluid that had been studied sufficiently at various operating temperatures in the United States to be used without extensive testing. Most of the work on Dowtherm A Rankine-cycle systems has been directed toward the space power plant, where the fluid must withstand temperatures of at least 650°F and preferably 700°F. However, naval power units encounter lower temperatures, and the design study was directed toward the use of Dowtherm A at about 600°F. At this temperature, thermal degradation should not be serious even for periods of as long as 5 years.

To decrease the overall size of the power unit, a new system configuration was evolved.[3] It appears that both the cost of fabricating the isotope capsules and the size and weight of the heat block–shield assembly can be decreased by increasing the diameter of the fuel capsules and the length with a corresponding decrease in the number of fuel capsules from 19 to 7, compared to those in the Phase I design. Low-carbon iron was selected as the shield material, and a heat block–shield assembly was evolved (Fig. 2) which will satisfy not only the requirements of the organic Rankine-cycle

*Program Director, Reactor Division, Oak Ridge National Laboratory.

†For the U. S. Atomic Energy Commission Division of Reactor Development and Technology and the Naval Facilities Engineering Command.

XUM



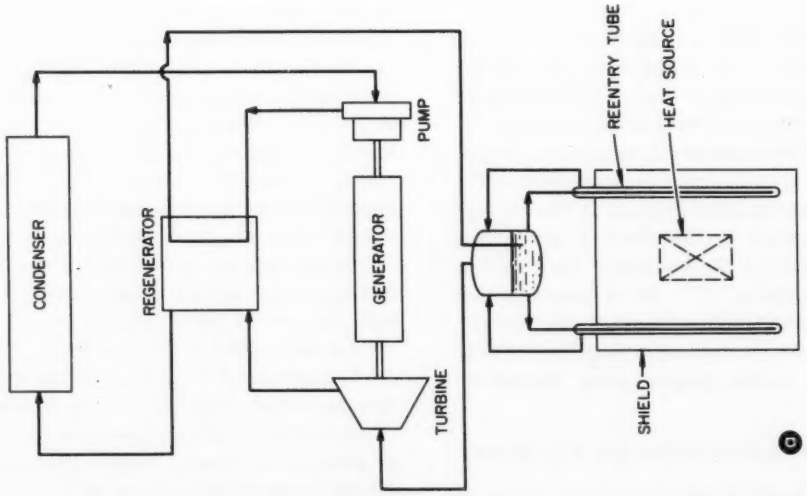


Fig. 1 Organic Rankine-cycle system: (*a*) flow diagram and (*b*) preliminary design.

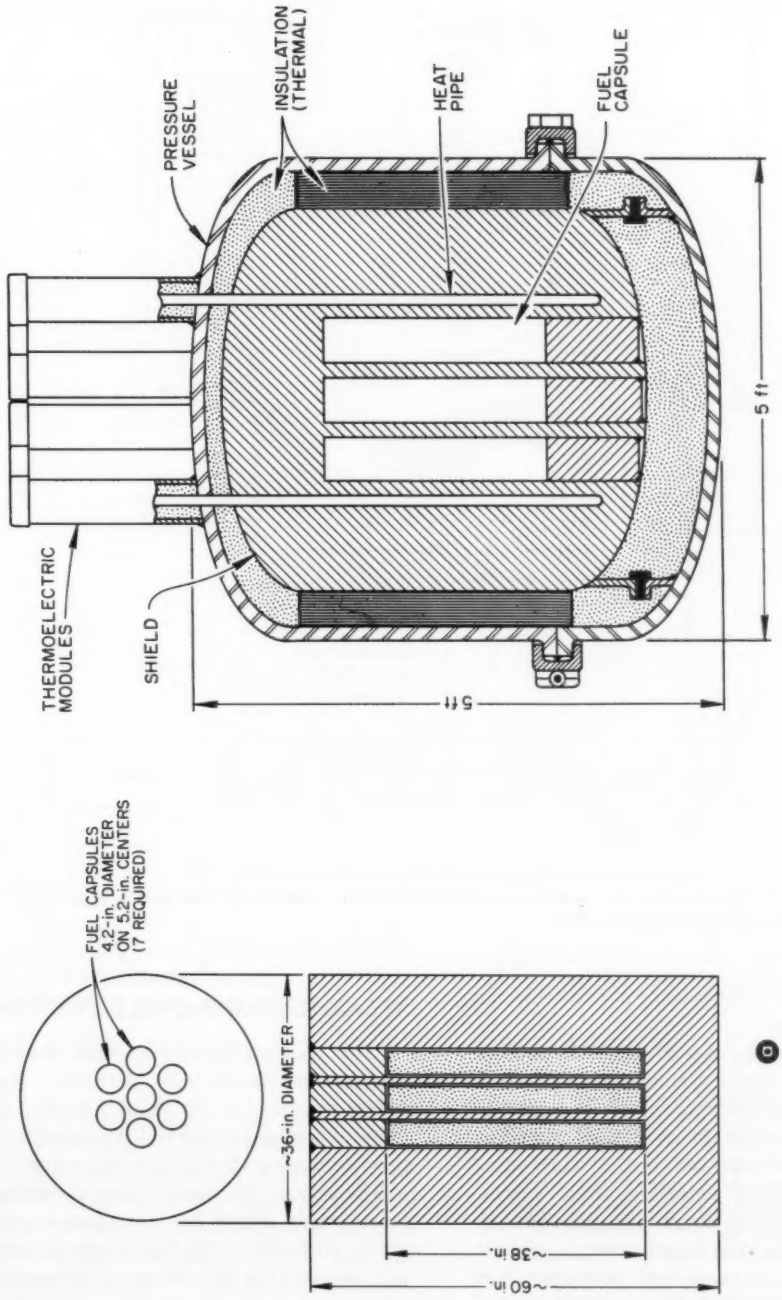


Fig. 2 Heat block–shield assembly: (*a*) diagram and (*b*) preliminary design.

XUM

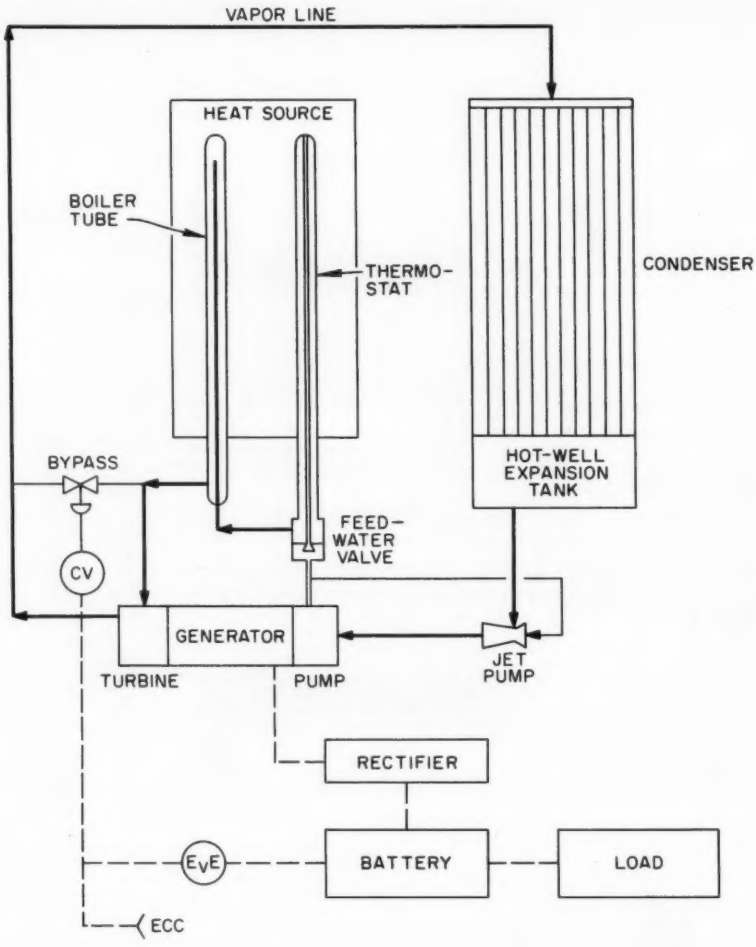


Fig. 3 Flow diagram of a small steam power plant with a radioisotope heat source, a once-through boiler, and a very simple control.

system but also those of the steam Rankine-cycle and thermoelectric systems.

An initial investigation of the thermal insulation–thermal fuse problem led to the hope that a ceramic foam type of thermal insulation could be chosen to give good thermal insulation at normal operating temperatures and yet melt out if the temperature should be increased 200°F above the design temperature. Tests of this material showed that this approach was not satisfactory, and a different concept—the use of a large number of layers of aluminum wire screen—was investigated. Preliminary results indicate that this screen should satisfy both the thermal-insulation and thermal-fuse requirements.

STEAM RANKINE-CYCLE SYSTEM

The principal problems, other than the turbine generator associated with the steam Rankine-cycle system presented in the Phase I study,[1] appear to be those of system control and the detailed performance characteristics of the reentry boiler tube. Preliminary studies indicate that there is a good possibility that an exceptionally simple but unorthodox control system can be used with a very high degree of reliability. One such system (Fig. 3) contains a thermostatically controlled valve in the line between the feedwater pump and the once-through boiler. Connections would be such that as the radioisotope decays and the heat-

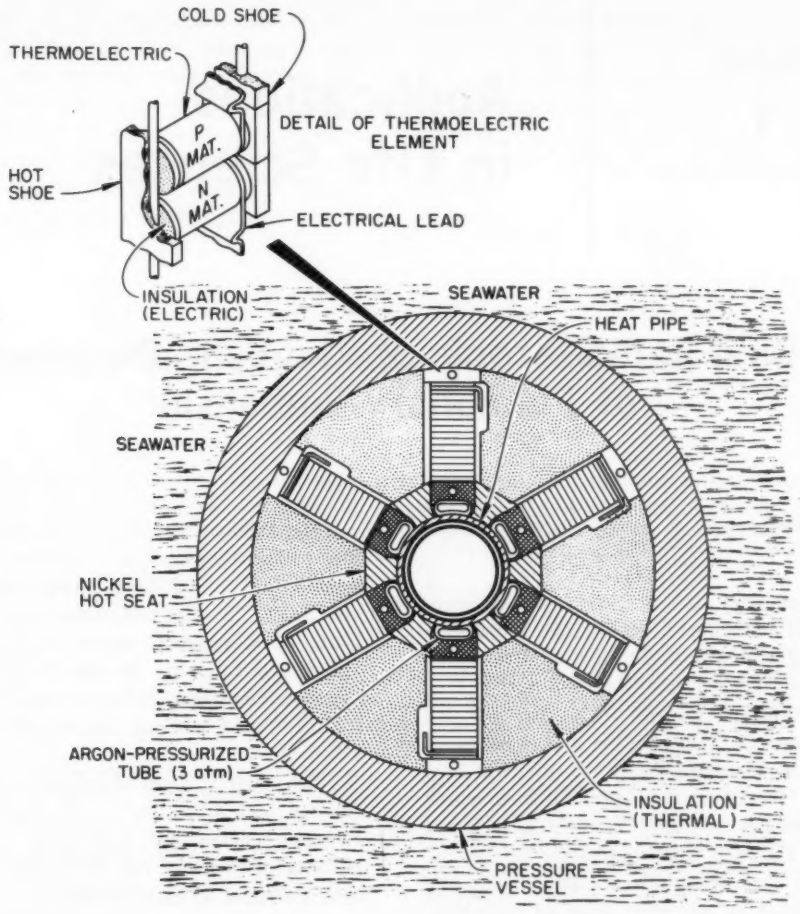


Fig. 4 Horizontal cross section through a thermoelectric module.

generation rate decreases, the valve would gradually close, decreasing the feedwater flow rate.

THERMOELECTRIC SYSTEM

All the thermoelectric-power-unit configurations presented in the Phase I study have serious shortcomings—they are either too large and bulky or have major assembly problems. A Los Alamos–developed wick structure for heat pipes was used as the basis for designing a modular thermoelectric-power unit that appears attractive from the standpoint of the principal criterions that have been evolved for naval isotope power units. A complete power unit consisting of a set of thermoelectric modules and heat pipes has been designed (Fig. 4) and is expected to serve as the reference design for the Phase II effort. (MG)

REFERENCES

1. R. M. Chapman, D. A. Patterson, et al. (Eds.), *A Report by the Panel on Energy Sources of the Committee on Undersea Warfare* [Washington, D. C., April 1967], National Research Council, Publication 1702, National Academy of Sciences, Washington, D. C., 1968; extracted in *Isotop. Radiat. Technol.*, 7(4): 449-451(Summer 1970).
2. R. A. Robinson, Isotopes Kilowatt Program, Task 1, Conceptual Design and Evaluation, USAEC Report ORNL-TM-2366, Oak Ridge National Laboratory, January 1970.
3. A. P. Fraas, Isotope Kilowatt Program Quarterly Progress Report for Period Ending March 31, 1970, USAEC Report ORNL-TM-3011, Oak Ridge National Laboratory, July 1970.

XUM

Section V

Isotopes and Radiation Technology

Applications in Life Sciences

Dual Radioisotopic Method for Diagnosis of Pulmonary Embolism*

Supplementary Keywords: *lung; medicine; ventilation; scanning; flow measurement; xenon-133; iodine-131; indium-113m.*

A simple and sensitive method to aid in the diagnosis of pulmonary embolism by distinguishing it from other causes of perfusion abnormality consists in determining both pulmonary arterial blood flow with ^{131}I or ^{113m}In and ventilation rate with ^{133}Xe. That the dual procedure is more accurate than the determination of blood flow alone was indicated by the results of tests on 20 subjects. Ten of these subjects had documented pulmonary embolism in which the embolic lung was underperfused and well ventilated, while in five patients with other pulmonary diseases, abnormalities of ventilation equaled or exceeded those of perfusion. Five were controls. The method is simple to perform and gives a low radiation exposure to the patient so that it may be repeated to follow the course of disease or the efficacy of treatment. The total time for perfusion scanning is 45 min and for ventilation scanning, 30 min or less.

The pulmonary arterial blood flow is determined from a perfusion scan. For this purpose, 300 μCi of ^{131}I-labeled human serum albumin macroaggregates or 3 mCi of ^{113m}In-labeled iron hydroxide particles of 25 to 50 μm diameter is injected intravenously. These particles are temporarily trapped in the alveolar capillaries and precapillary arterioles, and perfusion images are made, requiring 3 to 8 min (10^5 to 3×10^5 counts).

The regional ventilation is estimated with ^{133}Xe. The patient breathes out to residual volume and then breathes in to total lung capacity from a spirometer containing 50 mCi (5 mCi/liter) of ^{133}Xe gas in air. Since most patients inspire 2 to 5 liters of the radioactive mixture, 10 to 25 mCi of ^{133}Xe is transferred temporarily to the lungs. The patient holds his breath for 5 to 15 sec, and images are obtained with 10^5 counts.

The patients, either sitting up or lying down, were scanned with an Anger scintillation camera, using a diverging multichannel collimator. A posterior and both lateral views of the chest were obtained and, in some instances, an anterior view.

In all 10 patients with embolism, the perfusion pattern was less normal and uniform than the ventilation pattern (Fig. 1). In the five patients with other pulmonary diseases—primarily chronic obstructive pulmonary disease—the abnormality in the ventilation

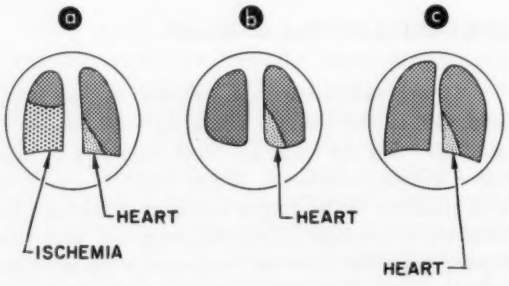


Fig. 1 Sketches of anterior views of three patients showing (*a*,*b*) perfusion and (*c*) ventilation scans.

*Abstract of paper by G. L. DeNardo, D. A. Goodwin, R. Ravasini, and P. A. Dietrich, The Ventilatory Lung Scan in the Diagnosis of Pulmonary Embolism, *New England Journal of Medicine* (in press).

pattern was equal to or greater than that of the perfusion pattern. The ventilation lung scan thus indicates whether the regional perfusion defects are associated with abnormal ventilation. In embolism without infarction the embolic lung area appears underperfused but well aerated. This effect is reflected on lung scans by relatively normal ventilation associated with significant perfusion abnormalities. In other pulmonary diseases the ischemic regions are also poorly ventilated. Although other conditions that might produce the pattern of normal ventilation with abnormal perfusion have not been precisely defined, theoretical considerations and limited empirical observations suggest that this pattern may be specific for pulmonary embolism.

(MG)

Radioisotopes and Rice

Supplementary Keywords: *material tracing; comparison; mutation; grain; agriculture; X-ray machine; accelerator; cobalt-60; nitrogen-15; phosphorus-32.*

With rice the staple diet of about half of mankind, the importance of any measures taken to increase crop yields and decrease production costs cannot be overestimated. Two recent publications of the International Atomic Energy Agency (Vienna, Austria) describe projects in this field:

Rice Fertilization, A 6-Year Isotope Study on Nitrogen and Phosphorus Fertilizer Utilization, Technical Reports Series, No. 108 (177 pp., $5.00).

Rice Breeding with Induced Mutations. II, Report of Meeting in Oiso, Japan, 12–14 August 1968, Technical Reports Series, No. 102 (124 pp., $4.00).

Both projects were carried out under the sponsorship of the Joint FAO/IAEA Division of Atomic Energy in Food and Agriculture and of the agriculture section of the IAEA laboratory at Seibersdorf, the participants being mainly scientists from the major rice-producing countries of the world. There were about 20 and 35 participants in the fertilizer and mutations conferences, respectively.

A unique feature of the fertilization project was the annual meeting of the participants to compare and discuss the results obtained from the most recent field, greenhouse, and laboratory experiments and to plan the program for the next growing season. The study consisted in field application of fertilizers labeled with ^{32}P and ^{15}N in various chemical forms, in different locations with respect to the plant-rooting zone, and at various times during the growing season and then determination of the amounts of these isotopes in the crops. This gave a direct measurement of the fertilizer uptake under field conditions. Crop yields were also determined.

The results of the fertilization study will allow more efficient utilization of fertilizer and an improvement in agricultural practices. For example, phosphate was more efficiently used when placed on the surface than when put either shallowly or deep into the ground. Superphosphate applied in nurseries had no effect on phosphorus utilization after transplanting, and late application and splitting of application slightly decreased phosphorus utilization. Nitrogen from ammonium sulfate, urea, or monoammonium phosphate–ammonium sulfate was utilized better when placed 5 to 15 cm below the surface at transplanting time than when placed on the surface, while sodium nitrate, ammonium nitrate, and nitric phosphate were inefficient sources of nitrogen. Late application was better than early, and the soil *p*H did not affect the nitrogen utilization.

The 1968 meeting on rice breeding was the fourth* meeting of participants on a program initiated in 1964 to increase quality and quantity of rice crops. Mutations induced by both radiation—^{60}Co gamma rays, fast- and thermal-neutron beams, and X rays—and chemicals were discussed. Detailed tables of data on mutant characteristics are presented in the proceedings.

(MG)

*See *Isotopes and Radiation Technology,* 6(3): 319 (Spring 1969) for a review of reports on earlier work.

XUM

Frostbite Evaluation with ^{131}I-RISA

Supplementary Keywords: *medicine; diagnosis; skin; tracer.*

A radioisotopic technique for evaluating frostbite has been reported* from Albany (N. Y.) Medical College. The procedure, as tested on New Zealand white rabbits, consisted in injecting 10 μCi of ^{131}I-labeled human RISA (radioiodinated serum albumin) into an ear vein and counting, at 5-min intervals, the activity in the animal's front paw, which had been frozen. The uninjured front paw and the paws of entirely normal animals were used as controls. The method was tested both immediately after exposure of the paw to cold and 24 hr later, since human frostbite cases are usually seen by a doctor after the damaged tissue has thawed.

Preliminary data showed a statistically significant difference in the radioactivity counting pattern in the damaged and undamaged paws (Fig. 1). Indications are that this method of detecting tissue damage—and thus of predicting tissue loss—could be useful in evaluating methods of treating frostbite. (MG)

*D. B. Kettelkamp, C. J. Bertuch, and P. Ramsey, Radioisotope (^{131}I RISA) Evaluation of Damage in Frostbite. An Experimental Study, *Journal of Bone and Joint Surgery*, 51-A(4): 717-727 (1969).

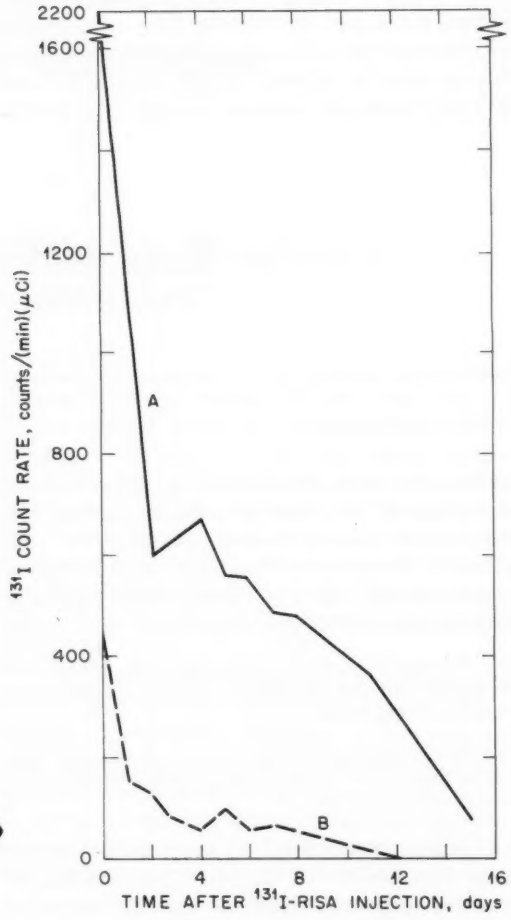


Fig. 1 Radioactivity count rate, per microcurie of ^{131}I injected, in paws of New Zealand white rabbits (*A*) damaged by freezing with resulting tissue loss and (*B*) undamaged.

NEUTRONS FROM ^{2}H AND ^{3}H MAY FIGHT CANCER*

Supplementary Keywords: *accelerator; medicine; therapy.*

The fusion of ^{2}H and ^{3}H may be the source of neutron beams for cancer therapy. A low-cost compact machine to deliver a 14-MeV neutron beam is being developed at the University of Wisconsin. The beam will attack anoxic cells that are resistant to X and gamma rays. The National Institutes of Health funded project is directed by Dr. Max L. M. Boone, head of the Radiotherapy Department of the University's hospitals, and Dr. Charles A. Kelsey, associate professor of radiology. Dr. Boone has achieved good results with neutron therapy at Hammersmith Hospital in London, but the cyclotron neutron source he used was expensive and unwieldy.

*From *Chemical and Engineering News*, p. 61, June 8, 1970.

Book Reviews

Molecular Radiation Biology, by Hermann Dertinger and Horst Jung, Heidelberg Science Library, Vol. 12, translated from the German by R. P. O. Hüber and P. A. Gresham, Springer-Verlag, New York, 1970 (237 pp., 365 references).

Supplementary Keywords: *review, technical; theory, applied; microbiology; industry, food; industry, pharmaceutical; tracer; hydrogen-3; carbon-14; phosphorus-32; sulfur-35.*

Many uses of ionizing radiation depend ultimately on the effect of radiation on materials at the molecular level. Dertinger and Jung review not only the theoretical bases of radiation effects but also some specific effects, e.g., the actions of radiation on enzymes and bacteria, which are of interest to the food and pharmaceutical processors, and the action of radiation on viruses, which is of interest to antitoxin manufacturers. Several types of applied radiation are considered—gamma, X, electron, proton, and C^{6+} (and ultraviolet). Likewise some discussion is included of the action of energy from radioisotope tracers—e.g., ^{3}H, ^{14}C, ^{32}P, and ^{35}S—along with the effects of O_2 and heat. As a basic review of the subject, this book should be useful to radioisotope users in general. (MG)

Radiation Sensitivity of Toxins and Animal Poisons, Panel Proceedings Series, Bangkok, May 19–22, 1969 (STI/PUB/243), International Atomic Energy Agency, Vienna, 1970 (118 pp., $4.00).

Supplementary Keywords: *industry, pharmaceutical; preparation, labeled material; industry, food.*

Many snake venoms, because of their protein nature, are relatively sensitive to radiation and can often be detoxified by an irradiation technique. Of interest to persons in many fields is the general review (111 references) of the effect of radiation on biological properties since other toxins of bacterial and plant origin are similarly affected. Specific subjects discussed by the Panel included radiation sensitivities of individual systems such as *Clostridium botulinum* toxins and cobratoxin. Not only theoretical aspects of detoxication but also possible practical applications were considered, e.g., detoxication of cobra venom for production of an antivenom. The results of investigations presented at the meeting indicate the feasibility of using ionizing radiation for detoxication of toxins and venoms of bacterial, fungal, and animal origin and its possible usefulness in the preparation of antivenoms. However, the Panel concluded that the elimination of bacterial toxins from foodstuffs by irradiation does not seem to be promising since the toxins in food are highly protected by other components present.

One paper discussed labeling of snake venom with various radioisotopes. In principle, all methods available for labeling proteins in vitro and in vivo could be applicable for labeling toxins and venoms. More attention should be paid to working out suitable methods for labeling toxins and venoms and to their use in biochemical, physiological, pharmacological, and immunological studies of toxin action and of antigen–antibody interaction. (MG)

Medical Radionuclides: Radiation Dose and Effects, (AEC Symposium Series, No. 20). Proceedings of a Symposium at Oak Ridge Associated Universities, Dec. 8–11, 1969, Editors: R. J. Cloutier, C. Lowell Edwards, W. S. Snyder, and E. B. Anderson. June 1970 (528 pp.; available from NTIS as CONF-691212 for $3.00).

Supplementary Keywords: *medicine; diagnosis; dosimetry; tracer.*

Ever since the introduction of radionuclides for diagnostic purposes, the trend has been to decrease radiation dosage to patient (and hazard to medical staff personnel) with increase in specificity and sensitivity of the test procedure.

At a December 1969 conference the history of dosimetry procedures was presented, and principles involved in modern dosimetry practices were discussed. Consideration was given to patient doses resulting from certain specific diagnostic procedures, e.g., cisternography using ^{131}I-labeled human serum albumin, ^{133}Xe techniques, and ^{3}H-labeled thymidine procedures. The effects of radioisotopic techniques on various organs and tissues—blood, kidneys, gastrointestinal tract, and bone and marrow—were presented, and the design of new radiopharmaceuticals and the future of radioisotopic diagnostic procedures were discussed. Radioisotopic therapy considerations were limited to effects of radioactive iodine therapy and polycythemia vera treatment with radioisotopes.

Approximately 150 persons, mostly from the United States, participated.

The printed proceedings of the conference became available within 6 months, and the editing, makeup, and printing are excellent. (MG)

XUM

Section VI

Isotopes and Radiation Technology

Safety

Shipping-Cask Evaluation*

By R. D. Seagrent

Abstract: *Radioisotope shipping-cask regulations and sources of information needed by the shipper are reviewed.*

Supplementary Keywords: *industry, transportation; bibliography; industry, nuclear energy; safety, container; phosphorus-33, krypton-85; strontium-90; molybdenum-99; curium-244.*

In January 1969 the U. S. Department of Transportation's (DOT) new packaging requirements for radioactive material went into effect. These regulations[1] are in substantial conformity with those of the International Atomic Energy Agency (IAEA).[2] Radioactive material is now classified into seven groups, depending on the radiotoxicity of the isotope concerned. Smaller amounts of more-toxic material and larger amounts of less-toxic material may be shipped in the same type of package. Shipping packages are now divided into two types: type A and type B. Type A packages are limited to small amounts of radioactive material, which, if released in the event of a package's being destroyed, would not have catastrophic consequences. Type B packages are for shipments of somewhat larger amounts of radioactive material and are designed to contain the radioactive material when subjected to a series of consecutive hypothetical shipping accidents.

Figure 1 shows a typical type A package, which is considered adequate containment for, for example, 1 mCi of most alpha emitters, 50 mCi of ^{90}Sr, 3 Ci of ^{33}P, or ^{20}Ci of ^{99}Mo, provided radiation requirements are met. This package is designed to meet what is termed "normal" conditions of transport. These include exposure to the equivalent of a 30-min cloudburst, followed by the equivalent of a fall off the tail gate of a truck, a 1-ft drop onto each corner of the package, the impact of a 13-lb steel rod from a height of 40 in., and a compression load five times the weight of the package for a period of 24 hr.

Figure 2 shows typical examples of type B packages, suitable for, for example, 20 Ci of most alpha emitters, 20 Ci of ^{90}Sr, 200 Ci of ^{33}P, 200 Ci of ^{99}Mo, or 50,000 Ci of ^{85}Kr. These packages are designed to meet normal conditions of transport and also to withstand a series of consecutive hypothetical accidents. The series of accidents are a 30-ft drop onto an unyielding surface, a 40-in. drop onto a 6-in.-diameter steel pin, exposure to a 30-min oil fire, and immersion in 50 ft of water.

Quantities of radioactive material larger than those specified for type B packages must be shipped in packages especially approved by the AEC and the DOT. Packages formerly shipped under the authority of a Bureau of Explosives permit can no longer be used.

REGULATORY REQUIREMENTS

During this century radiation regulations evolved as knowledgeable persons became aware of the hazards of radiation. Initially, they dealt with X rays and radium, but, with the advent of the nuclear-energy program, just prior to World War II, a whole new regulatory effort dealing with radiation safety came on the scene. Operating experience during the Manhattan Project made it apparent that regulatory direction of

*Presented at Radioisotope Production Technology Development Meeting at Oak Ridge, Tenn., June 2–3, 1970, sponsored by the USAEC's Division of Isotopes Development and the Atomic Industrial Forum.

†Isotopes Division, Oak Ridge National Laboratory.

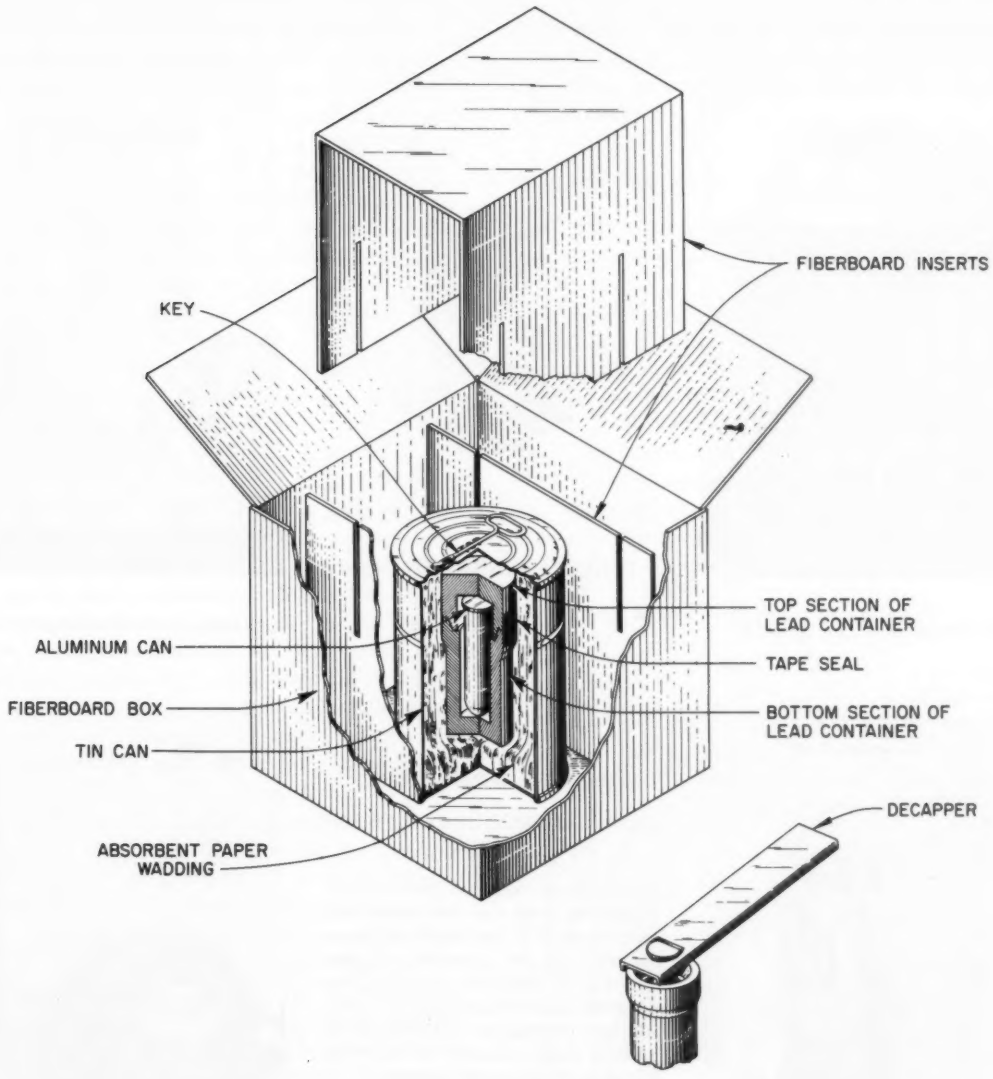


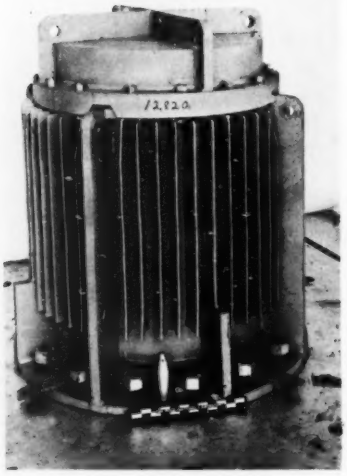
Fig. 1 Disposable container for solid materials (lead shielding, ¼ and ½ in.).

radiation safety was in the public interest, not only for the health and welfare of mankind but also for allaying fears and overcoming reluctance to accept this little-understood form of energy.

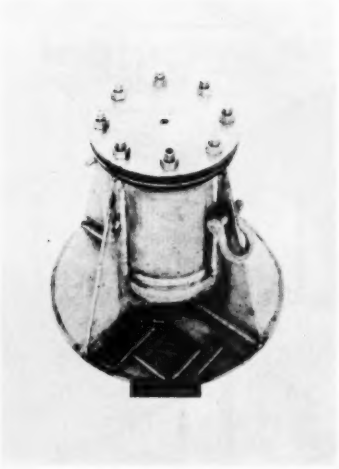
The AEC and the Public Health Service were initially instrumental in establishing standards for radiation safety. In recent years possibly every executive branch of the federal government and presidential commission, as well as officials of 50 states and many cities and counties, have had something to add to radiation-safety regulations. Trade organizations have developed tariffs, or agreements, which, although not regulatory, deal with radiation and radioactive material.

It is apparent that regulatory personnel at all levels of government are sensitive to the many warnings regarding the real and sometimes imagined hazards of radiation, and it is often easy to conclude that some regulations are born of fear, by well-meaning but not necessarily knowledgeable people. This fear of the

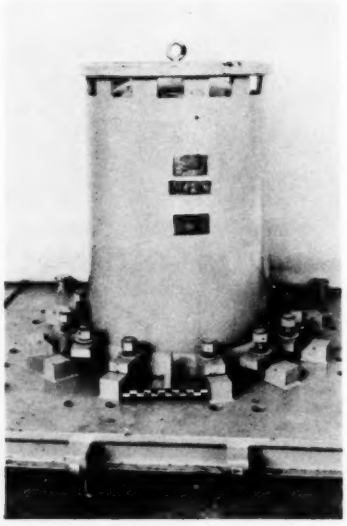
XUM



URANIUM-SHIELDED CASK



TUNGSTEN-SHIELDED CASK



DOUBLE-LEAD-SHIELDED CASK

RADIOACTIVE-GAS CYLINDERS WITH FOAMED-PLASTIC FIRE AND IMPACT SHIELD

SHIPPING CONTAINERS

ORNL ISOTOPES DEVELOPMENT CENTER

New shipping containers have been developed to meet the new safety standards of the U. S. Department of Transportation for the packaging of large quantities of radioactive materials. This is part of a continuing program to ensure reliability of shipping containers and to establish design standards for improved packaging of radioactive materials.

LEAD-SHIELDED CASK WITH FIRE AND IMPACT SHIELD

Fig. 2 Typical type B packages.

unknown has been instrumental in the development of the most highly regulated industry in our history.

The basic regulation on packaging, 49 CFR, includes the Hazardous Materials Regulations of the DOT. A second set of rules is found in Title 10, which contains the regulations set forth by the AEC, Part 71 of which is entitled "Packaging of Radioactive Material for Transport." Another set, Title 46, contains the Coast Guard regulations, Part 146 of which is entitled "Transportation or Storage of Explosives or Other Dangerous Articles or Substances and Combustible Liquids on Board Vessels."

For type A packaging, regulatory requirements are minimal. Essentially, the shipper certifies that his package is strong and tight and meets the requirements of normal conditions of transport.

Type B packaging is a different case. The user must furnish to the DOT proof that the package will withstand the series of four consecutive hypothetical accidents (drop, puncture, fire, and immersion). This proof may be either engineering evaluations, comparative data, or actual test results. If the Hazardous Materials Regulations Board of the DOT decides that the package complies with regulations and is indeed safe, it will issue a special permit, stating conditions of use and modes of transport to be used. In some cases the DOT will ask the Division of Materials Licensing at AEC Headquarters to review the evaluation.

Packages to contain quantities of radioactive material larger than type B quantities are handled in a still different manner. The AEC regulations require that a licensee submit an evaluation of such a package to the Division of Materials Licensing for approval. This evaluation must demonstrate compliance with all applicable requirements of 10 CFR 71. It is generally a formal engineering analysis. Let me point out that an analysis should cover the letter as well as the spirit of the regulation. A straightforward, honestly presented, fully documented evaluation of a package that is sincerely believed to be adequate will do much to eliminate the game of "20 Questions" that some regulatory groups are sometimes thought to play. After the AEC has issued a license amendment or other form of approval, a petition for a special permit must be submitted to the Office of Hazardous Materials of the DOT in the format of 49 CFR 170. This section of the regulations requires justification for a special permit, why the public interest would be served, and the basis upon which the petition would provide an adequate and reasonable degree of safety. The office makes a technical review of the petition and then forwards it to the administrators of the modes of transport involved. The Highway, Railroad, or Aviation Administration, as well as the Coast Guard, reviews the petition and either approves or disapproves it. If approved, a special permit is issued.

DEVELOPMENTS

The Division of Isotopes Development supports a continuing program of package design, development, and evaluation as part of the Source Safety Testing Program. The objective of this program is to evaluate radioactive-material packaging to determine whether it meets performance standards developed by the AEC, the DOT, and the IAEA. Since the Isotopes Division of Oak Ridge National Laboratory (ORNL) is responsible for all the laboratory's shipments of radioactive material, it handles and evaluates all types of packaging and has been instrumental in the development of several new concepts of package design. Figure 3 shows a

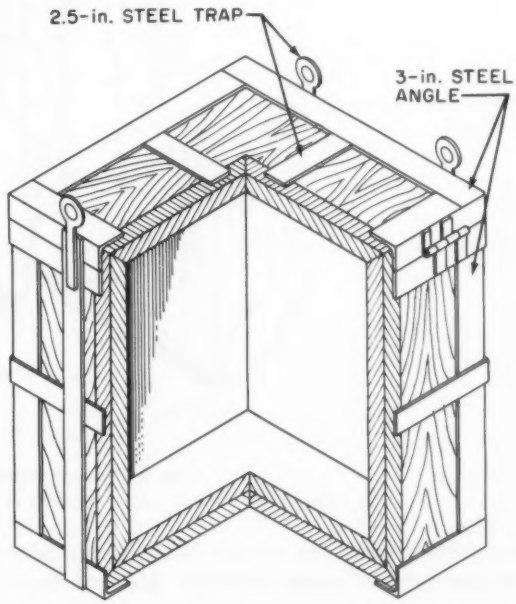


Fig. 3 Laminated-fir-plywood and maple fire and impact shield.

laminated-fir-plywood and maple fire and impact shield for transporting lead-shielded casks. Figure 4 shows a tungsten-shielded cask for material requiring up to 4 in. of lead shielding. The shield is an isostatically pressed and sintered tungsten alloy. A third design is a double-

XUM

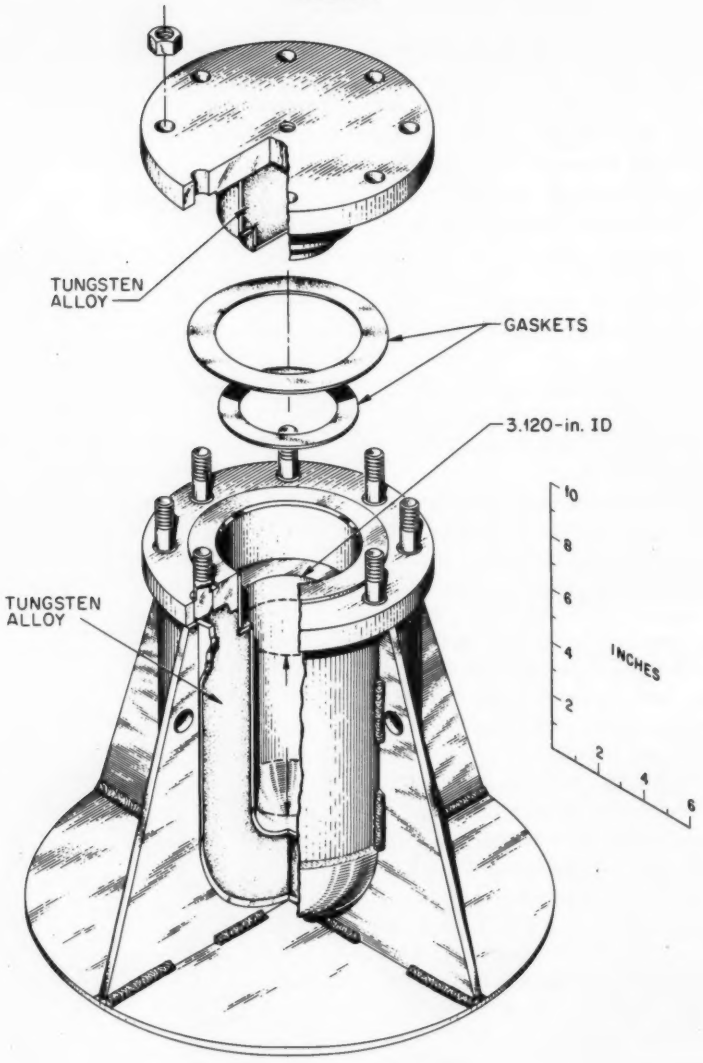


Fig. 4 Tungsten-shielded cask (380 lb).

lead-shielded cask. The purpose of this design is to improve fire and impact resistance. A fourth design utilizes a laminated-uranium construction as the radiation shield and also offers improved fire and impact resistance. Figure 5 shows a new design concept being developed for shielding fast neutrons emitted from some of the transuranium elements. The shielding consists of the lithium hydroxide monohydrate form, which offers approximately the same shielding effectiveness as water. Fire resistance is accomplished by transpiration cooling, the material being about half water.

DESIGN

Prior to designing a new package or evaluating an old one, a user should first examine the DOT regulations to determine if there are packages that have already been approved for use in transporting the material under consideration. Such packages are referred to as "specification containers." The DOT regulations may be purchased from the Superintendent of Documents, U. S. Government Printing Office, Washington, D. C. 20402, as Title 49 of the *Code of Federal Regulations.*

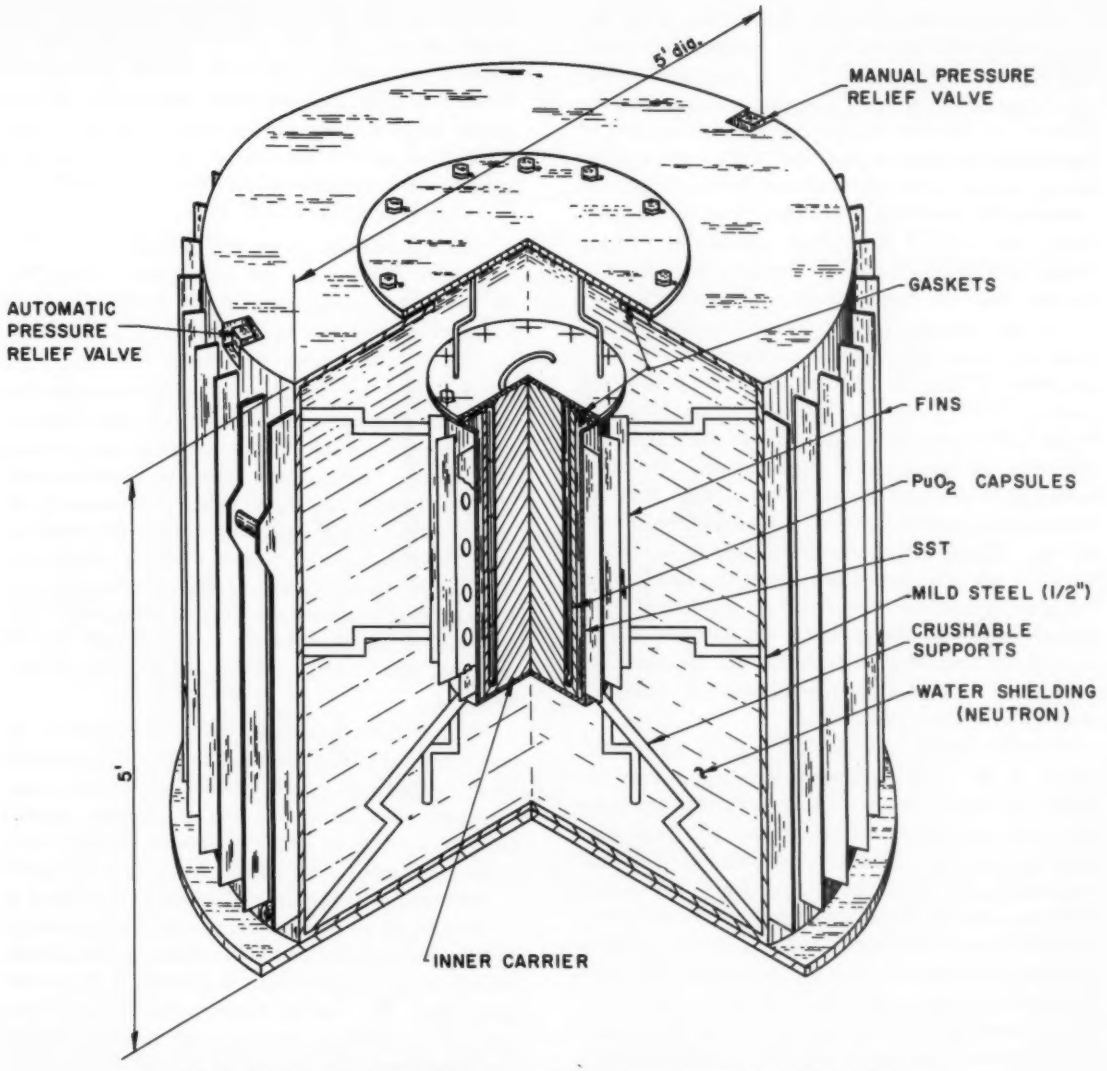


Fig. 5 Shipping carrier for bulk shipment of PuO_2 microspheres and fueled PuO_2 capsules.

If there are no specification containers that fit his need, the user should then examine the *AEC Directory of Shipping Containers*, assembled by the Division of Construction, USAEC, Washington, D. C. 20545. This directory also may be purchased from the Superintendent of Documents. Many of the packages listed in this directory have been approved for use under the authority of a special permit and require only the owner's permission and registration by the potential user with the Office of Hazardous Materials for their use.

If a package must be designed, the user may be interested in examining the *Cask Designers' Guide*, issued by the Nuclear Safety Information Center[3] at ORNL. This guide, developed under the sponsorship of the Division of Reactor Development and Technology, contains information a designer needs to ensure that his package meets the performance standards required by the appropriate federal regulations. It may be purchased from the National Technical Information Service, Springfield, Virginia 22151 (see the inside front cover of *Isotopes and Radiation Technology*).

XUM

Another source of design information is the Nuclear Safety Information Center's storage of document abstracts on magnetic tape at the Computing Technology Center in Oak Ridge. This Center operates a routine program of selective dissemination of information to individuals according to their particular interest. It has issued an *Indexed Bibliography on Transportation and Handling of Radioactive Materials*,[4] which contains many abstracts of documents concerning package design and evaluation. This information is available at no cost from the Nuclear Safety Information Center.

A new package design or an existing package evaluation must first meet the requirements of normal conditions of transport. Lifting devices, tie-downs, and package closures must be adequate to withstand the rough handling that packages receive in rail-, truck-, and airfreight depots as well as in transit. The mere existence of a radioactive label on a package does not necessarily guarantee that it will be handled like a crate of eggs. Snatch lifting, accidental falls from loading docks or tail gates, and load shifting are examples of transport conditions that must be considered. The primary aims of package design are to shield and to contain radioactive material when the packages are exposed to the wide range of environmental conditions as specified in the regulations.

Several avenues may be used to meet the requirements of the consecutive hypothetical accidents. As shown in Fig. 2, packages may be placed in fire-resistant outer containers that have impact resistance, e.g., steel-reinforced wooden cases or steel drums filled with vermiculite, fiberboard, or foamed plastic. The design of impact and fire shields is well understood since they have been tested and accepted internationally. Another concept of package design is the assumption that outer shells will rupture or be punctured as a result of the impact accidents. In this case loss of shielding may occur in the subsequent 30-min fire. Figure 6 shows a lead-shielded package based on a three-shell wall concept. The design provides inner and outer shells plus a third shell that is positioned approximately 2 in. inside the outer one; this arrangement provides for two separate chambers to contain the lead shielding. Under accident conditions, breaching of the outer shell and subsequent loss of the outer layer of lead would not necessarily cause the cask to fail the required tests. The shielding effectiveness would not be substantially reduced, and the loss of lead would create an air gap that would decrease the effective heat input to the inner cavity of the package.

As shown in Fig. 7, a similar concept, in which puncture of the outer shell may be allowed in an accident, is utilized in several French packages. A layer of wet plaster, with 26% free water, is poured between a lead shield and the outer shell. If these packages are involved in fires, the outer shells perforate by virtue of fusible plugs and the plaster dries, forming an insulating layer around the lead shield. Results of tests indicate that the layer offers adequate protection in case of an impact followed by a fire.

The UKAEA has patented (U. S. Patent 3,432,666) a fire shield that utilizes the evaporative cooling effect of the thermal decomposition of hydrated sodium borate, better known as Twenty Mule Team Borax. This decahydrate contains 48% water.

Since packages utilizing lead as radiation shielding have poor thermal-accident resistance, many designers are looking at reinforced concrete, steel, and uranium as answers to regulatory requirements. These materials offer solutions to specific shielding or transport problems. Certain types of concrete offer neutron shielding; steel, although not so effective a gamma shielding as lead, has excellent impact and thermal resistance; and uranium, with twice the shielding effectiveness of lead, is a leading contender with its impact and thermal resistance and with the reduced weight of equivalent shielding.

Heat transfer is a prime design consideration for radioactive-material packaging. Not only must packages remain effective in 130°F ambient air, but they must withstand solar heating as well as dissipate internal decay heat. As in most equipment design work, trade-offs have to be made. A package insulated to withstand a 30-min fire will naturally be limited as to the amount of thermal decay energy it may safely contain. Packages utilizing metal shielding, but without insulation, are excellent for the dissipation of internal decay heat. The use of cooling fins on the outer shell of a package increases the thermal dissipation capabilities. The amount of thermal decay energy that a package will effectively contain must be determined in order to get regulatory approval.

FABRICATION

The fabrication of packages should be well documented, and materials should be ordered by specification. Shop practice should be by appropriate codes, such as the ASME Pressure Vessel Code and the Standards of the American Welding Society. Nondestructive testing should be specified. Quality-control procedures developed by the Department of Defense and NASA are rapidly being recognized by AEC and

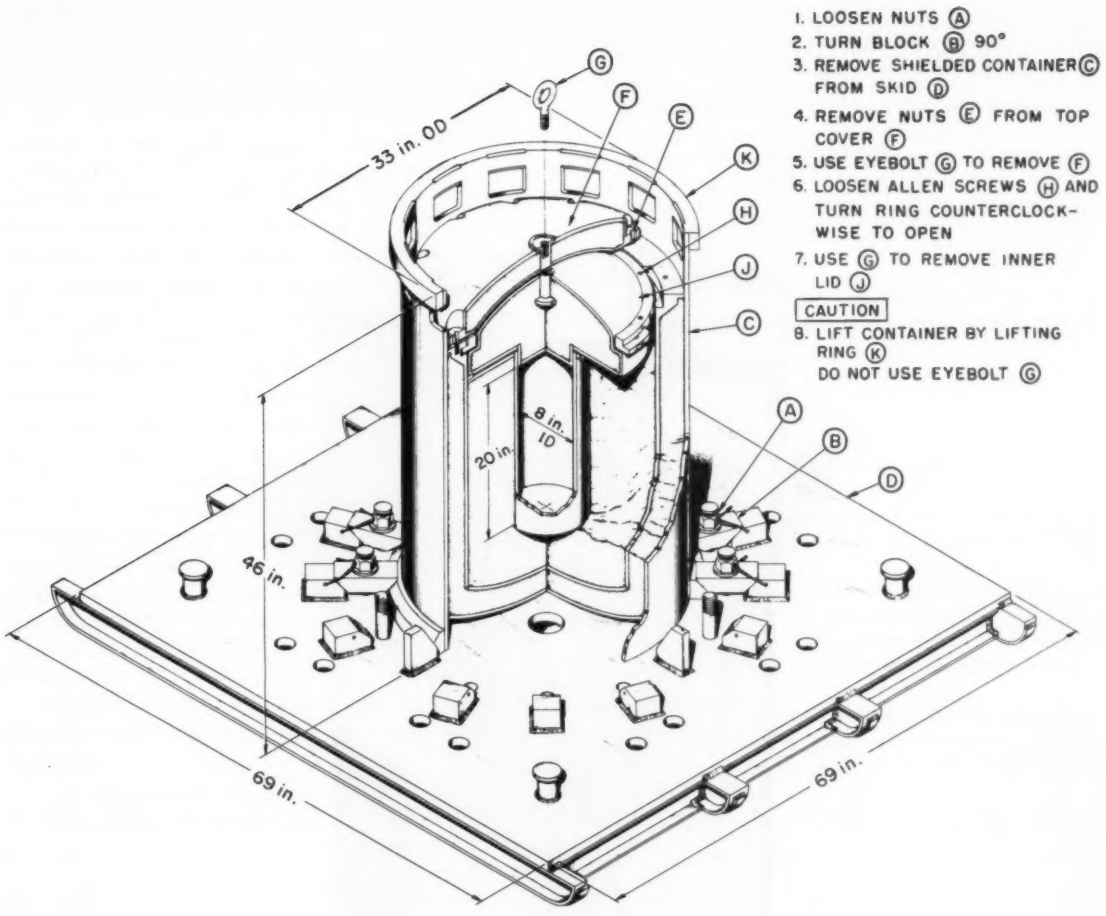

1. LOOSEN NUTS (A)
2. TURN BLOCK (B) 90°
3. REMOVE SHIELDED CONTAINER (C) FROM SKID (D)
4. REMOVE NUTS (E) FROM TOP COVER (F)
5. USE EYEBOLT (G) TO REMOVE (F)
6. LOOSEN ALLEN SCREWS (H) AND TURN RING COUNTERCLOCK-WISE TO OPEN
7. USE (G) TO REMOVE INNER LID (J)
CAUTION
8. LIFT CONTAINER BY LIFTING RING (K)
DO NOT USE EYEBOLT (G)
33 in. OD
8 in. ID
20 in.
46 in.
69 in.
69 in.

Fig. 6 Double-envelope carrier.

DOT regulatory personnel as standards and guides in evaluating assembly proficiency in the fabrication of packages.

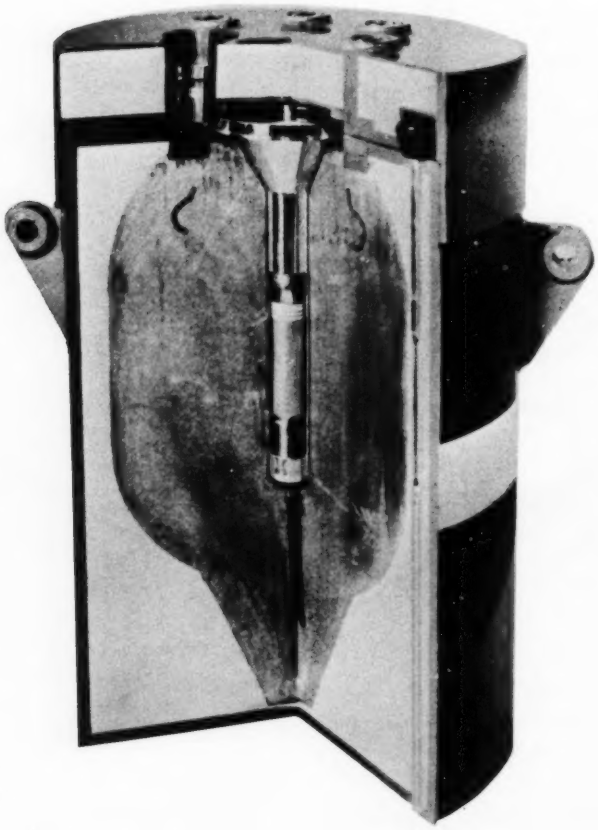
TESTING

Over the past 10 years, extensive package testing has been carried out both in this country and abroad. This testing is well documented in the literature, and the information is available from the references in the bibliography on transportation mentioned above. It is highly probable that a search of the literature would reveal comparative test data that are applicable or can be extrapolated to apply to most existing packages and packages to be fabricated in the near future. Prior to testing a package, the comparative data approach could be used as a means of meeting regulatory requirements, i.e., use the test data of a package design that is similar or equal to the design under consideration. An engineering evaluation of a package to withstand hypothetical accidents, although more costly, will generally suffice. In the case of novel or unusual packages, documented tests on a prototype are generally necessary to answer the questions and alleviate the doubts raised by regulatory personnel. A compendium of package-testing facilities under AEC control has been issued[5] by and is available from the Division of Construction, USAEC, Washington, D. C. 20545. Information may be obtained from this division on the availability of these facilities and on pricing.

XUM

CONTAINERS DE TRANSPORT
POUR RADIO-ÉLÉMENTS ARTIFICIELS
(Modèle P)

ISOTOPE STORAGE AND
TRANSPORT CONTAINERS
(Model P)



DESTINATION

Ces containers sont destinés au transport et au stockage de matière radioactive, contenue dans un tube standard à capuchon vissé ou soudé.

PURPOSE

These containers are designed for the transport and the storage of isotopes kept in a standard box closed by a screwed or welded plug.

Fig. 7 Example of French shielded package.

APPROVAL

The request for approval by the regulatory bodies for packages should be as broad as possible with regard to both present and possibly future conditions of use. Except in unusual cases, the user should not let himself be hamstrung by requesting approval for specific curie quantities of specific radioisotopes. For larger than type B quantities, gram quantities or thermal-watt quantities should be requested, e.g., 100 W of any solid, nonfissile radioisotope. Some regulatory personnel are reluctant to give approval on this basis, but many of the packages now in use were approved on this broad-coverage basis. Disregarding the difference in radiotoxicity and shielding requirements, it stands to reason that a package that will contain 100 W of ^{60}Co will just as effectively contain 100 W of ^{244}Cm.

After a request for package approval has been made, instant action by regulatory bodies should not be expected. Generally it will take from 3 to 4 months to physically move the paper through the various regulatory agencies. The service is speedy when you consider that the decisions are serious ones that will affect the health and welfare of the people of this country.

In closing, permit me to quote from a letter from one of the AEC contractors regarding the evaluation of packaging:

> In recent months, the public has shown an increasing concern about plans for the shipment of hazardous materials across our country. This concern has been demonstrated in the investigation of the movement of chemicals from the Rocky Mountain Arsenal. The Vermont Nuclear Power Town Meeting, held at the University of Vermont, and the Symposium on Nuclear Power and the Public sponsored by the University of Minnesota both aired the serious concerns of the citizenry for the possible increase of radiation and pollution of the environment from nuclear oriented enterprise. The public interest and the future of the industry demand that we take all reasonable action to verify our work.

I believe that this statement echoes the prevailing sentiment throughout the nuclear-energy field. (MG)

REFERENCES

1. Title 49, *Code of Federal Regulations* (CFR) Parts 170–190.
2. Regulations for the Safe Transport of Radioactive Materials, 1967 Edition, Safety Series, No. 6, International Atomic Energy Agency, Vienna.
3. Nuclear Safety Information Center, Cask Designers Guide: A Guide for the Design, Fabrication, and Operation of Shipping Casks for Nuclear Applications, USAEC Report ORNL-NSIC-68, Oak Ridge National Laboratory, February 1970.
4. Nuclear Safety Information Center, Indexed Bibliography on Transportation and Handling of Radioactive Materials, USAEC Report ORNL-NSIC-33, Oak Ridge National Laboratory, June 1967.
5. USAEC Container Testing Facilities (no document number).

XUM

Section
VII
Isotopes and Radiation Technology

Isotopes Around the World

Developments Abroad on Radioisotope-Powered Cardiac Pacemakers*

By Martha Gerrard

Supplementary Keywords: *energy source; medicine; therapy; plutonium-238; promethium-147; safety; heart; nuclear battery; conversion, electric; France; England; Australia; Switzerland.*

FRANCE

On Apr. 27, 1970, at the Broussais Hospital in Paris, a cardiac pacemaker (Fig. 1) that uses ^{238}Pu as the energy source was implanted[1,2] in a 58-year-old woman. The second French patient received an implantation in June.[3] The stimulator is 7 cm in diameter and 3 cm thick. The series now being constructed has a 23-mm-diameter generator, and the stainless steel has been replaced with titanium, so that the stimulator thickness is decreased and the weight is only about 160 g. The heat source is a 150-mg ^{238}Pu tablet, whose 87-year half-life gives the apparatus a useful life of about 10 years, compared with less than 2 years for cardiac stimulators using chemical batteries. The source is 9 mm in diameter and 10 mm high, and the helium expansion volume is 60 mm^3. The thermal power is 75 mW. It is doubly encapsulated—one capsule of tantalum and one of platinum, each 1 mm thick and electron welded.

The sealed source assembly and the thermoelectric converter—two rod-shaped bismuth telluride semiconductors—are inside an electron-welded stainless-steel capsule, 1 mm thick and 27 mm in diameter. The electric power is 200 μW at 0.5 V. This power is fed to an electronic circuit that uses 160 μW, with a useful life of more than 10 years. The loss through decay is 0.5 mV per month. The electrodes are epoxy clad. The generator has undergone prolonged and severe mechanical and thermal tests, and numerous safety tests have been made on the sealed capsule—leak tightness, shock, crushing, and fire resistance.

The electronics include a hysteresis-type pacemaker relay with magnetic triggering. The implanted stimulator delivers to the patient's heart pulses of 0.92 msec at 6.8 V with an energy of 41.6 μJ. The measured stimulation threshold was 0.54 μJ with myocardiac electrodes implanted on the right ventricle (xiphoumbilical path). The pulse frequency corresponds to a period of 816 msec, or 73 per minute.

At contact with the stimulator, very close to the ^{238}Pu, the gamma and neutron doses are 1.9 and 1.2 mRems/hr, respectively. On the patient's skin—an average of 21 mm from the stimulator surface—these doses are 0.25 and 0.17 mRem/hr. Two dogs have carried similar sources for 1 year without any significant biological changes being noted. Tissues in contact with the stimulator are heated $<0.1^{\circ}C$ above normal.

The myocardial electrode wires implanted in the patient have undergone tests in an accelerated test unit. A single-thread platinum wire irradiated in nonjoined spirals underwent 332 million flexions with a 7-mm radius of curvature and a 45° angle without breaking, while all other types of wires used for pacemakers had already broken.

The stimulator implanted in the patient is checked every month. The stimulator delivers a pulse only when

*This subject was introduced briefly in *Isotopes and Radiation Technology*, 8(2): 245 (Winter 1970–1971).

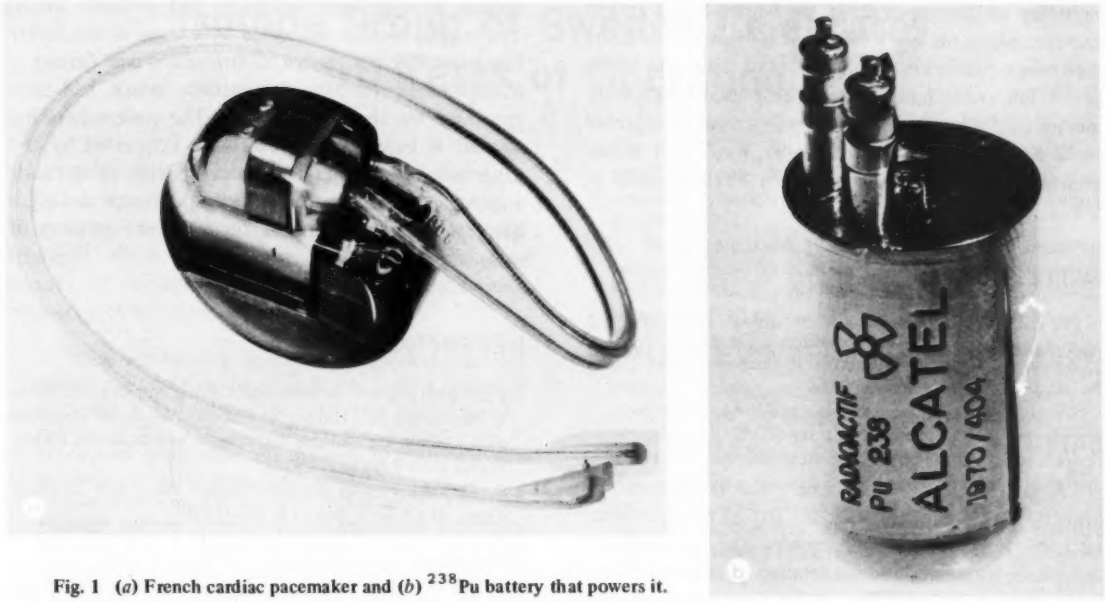


Fig. 1 (*a*) French cardiac pacemaker and (*b*) ^{238}Pu battery that powers it.

the beat of the heart itself is below the stimulator control threshold.

The ^{238}Pu source was developed by René Berger and René Boucher, Commissariat à l'Énergie Atomique, Fontenay-aux-Roses, and the thermoelectric converter, by M. Alais, Société Alcatel, Paris. The electronic circuits and controls were developed by Pieter Mulier, Medtronics, Minneapolis, Minn., USA, who now market conventional pacemakers and have reached an agreement[4] with Alcatel to market the ^{238}Pu pacemakers on an exclusive basis, possibly by 1975 (pending USAEC approval). Animal experimentation and clinical application were done by Professor Armand Piwnica, with Professor C. Dubost, Hôpital Broussais, Paris.

UNITED KINGDOM

On July 15, 1970, a radioisotopic cardiac pacemaker was successfully implanted in a woman at the National Heart Hospital in London. At the end of July, another such pacemaker was implanted in a 56-year-old man, the first male patient, who had previously had five conventional pacemakers.[5] The new pacemaker is designed to maintain, for at least 10 years, the heartbeat of patients suffering from heart block, while conventional—chemically powered—pacemakers must be replaced every 2 years. About 1300 conventional pacemakers are implanted in new patients in Great Britain every year. The human radioisotopic-battery implantations followed an extended period of laboratory trials and then actual implants in three dogs (two in London and one in Glasgow).

The power source of the British pacemaker is 180 mg of ^{238}Pu, the heat from which generates electricity by means of miniature thermoelectric semiconductors. The source is sealed in a capsule with dimensions of only a few millimeters and designed to withstand the maximum credible accident, including intense heat and a crushing force of 2 tons. The capsule is further encased in stainless steel, to form a completely sealed unit 2 in. long and 0.5 in. wide, which fits easily between the thumb and forefinger when handled.

The British device was developed through the combined efforts of scientists at the Atomic Energy Research Establishment at Harwell and doctors at the Institute of Cardiology and the National Heart Hospital, with considerable financial support from the Department of Health and Social Security. It is believed to be more efficient and less expensive than the French and American versions.

AUSTRALIA

The Nuclear Research Centre at Lucas Heights is assessing the possibilities of radioisotopic pacemakers in collaboration with the National Heart Foundation.[6]

XUM

Contrary to developments in the United States and in Europe, where mainly ^{238}Pu heat sources are used, the Australian concept is based on ^{147}Pm, alternate layers of ^{147}Pm and silicon crystals being used to generate electricity.[7] The power of the heat source is expected to be about 200 μW. The developer, F. C. Gatt, hopes eventually to be able to generate a 40-μA current at 5 V.

SWITZERLAND

A human implantation of a radioisotope-powered pacemaker is planned[8] in Switzerland for some time in 1970.

SAFETY

A joint group of experts has been established[9] to draw up safety guidelines for the design and construction of radioisotopic pacemakers and to examine technical, legal, and administrative problems arising from their wide use. The group, composed of specialists on the safety of nuclear pacemakers from the ENEA Study Group on Isotopic Batteries, Canada, United Kingdom, and United States and members of the ENEA Health and Safety Committee, met in June 1970 to investigate problems created by the use of the new pacemakers. For example, how will the plutonium battery hold up in an airplane crash, accidental cremation, or other accidents? The need for such study is indicated by, to mention only a single incident, the difficulty experienced by France's first nuclear pacemaker recipient when she tried to visit Spain. It took a special French–Spanish agreement to permit the trip.[3]

The Director General of the ENEA has asked the governments of the six countries involved in the study group (Austria, France, Germany, Spain, Sweden, and Switzerland) to allow persons with radioisotopic pacemakers to enter their territories and to travel freely. The request was accompanied by a copy of the *Safety Guidelines for the Design, Construction and Testing of Radioisotopic Cardiac Pacemakers,* which had been approved by the study group. The pacemakers implanted in France and those to be implanted by the other countries represented comply with these guidelines, which give engineering-design guidance and regulate administrative measures, including the recovery of radioisotopic sources.

REFERENCES

1. First Implantation of a Nuclear Cardiac Stimulator Ever to Be Implanted in a Human (in French), *Newsletter* (Information Bulletin on Isotopic Generators and Batteries, ENEA, Paris), 1(1): 2 (June 1, 1970).
2. P. Laurens, French Nuclear-Powered Pacemaker Program, *Trans. Amer. Nucl. Soc.*, 13: 508 (1970).
3. ENEA Looking at Travel Problem of People with Nuclear Pacemakers, *Nucleonics Week,* July 9, 1970, p. 8.
4. Medtronics Inc. Has Reached Agreement, *Nucleonics Week,* July 9, 1970, p. 8.
5. Nuclear-Powered Heart Pacemakers, *Atom,* No. 163: 100 (May 1970); Nuclear-Powered Pacemaker, *Atom,* No. 166: 166-167 (August 1970).
6. Nuclear Pacemaker Also Developed in Australia, *Newsletter* (Information Bulletin on Isotopic Generators and Batteries, ENEA, Paris), 1(1): 4-5 (June 1, 1970).
7. Isotope News from Australia, *Nucl. News,* 13(8): 35 (1970); also in *At. Energy Aust.*, 13(1): 37 (January 1970).
8. A. Senn, Department of Surgery, Anna-Seiler-Haus/ Inselspital, Bern, Switzerland, personal communication, Sept. 19, 1970.
9. ENEA Joint Group of Experts to Prepare International Standards for Radioisotopic Pacemakers, *Newsletter* (Information Bulletin on Isotopic Generators and Batteries, ENEA, Paris), 1(1): 5 (June 1, 1970); ENEA Ad Hoc Group of Experts on the Safety of Radioisotopic Pacemakers Meets in Paris, 24th–26th June, 1970; also, International Travel for Bearers of Plutonium-Powered Cardiac Pacemakers, *Newsletter,* 1(2): 4 (Sept. 15, 1970).

Isotope Group of Sweden Celebrates 10 Years of Operation

On May 26, 1970, Isotope Techniques Laboratory (ITL) of Stockholm observed its tenth year of service to industry. Seligman, of the IAEA, was a featured speaker.[1] He briefly reviewed the history and economics of isotope use and predicted a continuing expansion in this field. He said, in part:

> There will be a big increase in the use of isotopes and radiation for the well-known applications and a number of new ones will develop. If I may make a prediction—companies like ITL are still at the beginning of an exponential graph which for the next 10 years or even a generation will not change its direction.
>
> Let us sum up with what the future will bring for large radiation sources. If we leave aside the already established industries, like sterilization of medical products and cross linking of polyethylene as well as the curing of paint, we can foresee the curing of rubber latex, the butadiene grafting of polyvinylchloride. The sulphoxidation of alkanes to produce detergents, although not looking too good, has already been claimed to be a success by at least one country. The copolymerization of ethylene and carbon monoxide might give new polyketones and the copolymerization of ethylene with vinyl acetate might result in novel elastomers. A new field may be the production of novel ion-exchange materials from polyethylene or Teflon by grafting.
>
> On the sterilization front, we can prevent the formation of algae growth, for example, in cooling water. It may also have an influence in the fermentation industry. Some work is proceeding on transmutation doping for p/n junctions to the advantage of microcircuitry.
>
> Radiation-chemical synthesis—like the chlorination of methane, toluene, or benzene—may at last become an economic proposition; also the oxidation of toluene is a possible one. The novel use of sensitizers might not only reduce the dose necessary for a certain process, but it might also have a directional effect on the preference of radiation-induced reactions. This could lead in the further future to the solid establishment of a radiation chemical industry which I predicted 15 years ago!

(MG)

REFERENCE

1. H. Seligman, Industrial Isotope Application, Yesterday, Today and Tomorrow (English), *Isotopnytt*, No. 42: 1-8 (July 1970).

XUM

Section VIII

Isotopes and Radiation Technology

Miscellaneous

Availability of Isotopes and Services

ORNL ENRICHED-STABLE-ISOTOPE INVENTORY

Recent additions to the Oak Ridge National Laboratory (ORNL) enriched-stable-isotope saleable inventory include the following:

Isotope	Purity, %	Amount available, g
^{17}O	10.0	0.5
^{18}O	98.1	36.7
^{50}Cr	88.0	2.8
^{138}Ce	11.3	0.5
^{142}Ce	83.1	8.9
^{154}Gd	99.3	2.6
	98.3	0.3
^{160}Dy	78.9	1.5
^{162}Er	27.3	0.8
^{185}Re	96.2	8.2
^{187}Re	99.2	4.9

ISOTOPIC SEPARATIONS

Stable

During the fall of 1970, the stable isotopes of cadmium, gadolinium, iron, mercury, and tin were being separated on a 5-day around-the-clock basis in 21 beta-type calutrons and three 255°-modified calutrons. The cadmium isotope separation, made in the 255° separators, replaced a neodymium separation on Sept. 9, 1970, and was scheduled for completion about Mar. 15, 1971. The gadolinium isotope separation, which also started Sept. 9, 1970, was scheduled to proceed in three 180° calutrons until about the middle of March 1971. The tin isotope separation continued in eight calutron tanks until about Nov. 1, 1970, when it was replaced by a gallium isotope separation. This separation was scheduled for approximately 3 months. Estimates are given in Table 1 for the chemical recovery and mass analysis of each isotope collected and are calculated from parameters established in previous separations. The iron and mercury separations will continue until current requirements are satisfied.

The four separators in Building 9731 (two beta calutrons with 24-in. radius and two alpha machines with 48-in. radius) were restored to service following

Table 1 Additions to the Inventory During the Next 6 Months

Isotope	Lot No.	Estimated recovery, g	Estimated mass assay, at. %
^{121}Sb	NN 164502	50	99.5
^{123}Sb	NN 164601	35	98
^{125}Te	NS 166201	46	95
^{126}Te	NS 166301	112	98
^{142}Nd	OU 1794	235	96
^{143}Nd	OU 1795	110	80
^{145}Nd	OU 1797	73	75
^{148}Nd	OU 1799	63	88
^{150}Nd	OU 1800	55	95
^{112}Sn	OT 1784	23.5	>80
^{114}Sn	OT 1785	17	60
^{115}Sn	OT 1786	9.8	30
^{117}Sn	OT 1788	235	80
^{118}Sn	OT 1789	175	95
^{119}Sn	OT 1790	235	85
^{120}Sn	OT 1791	225	98
^{122}Sn	OT 1792	120	90
^{124}Sn	OT 1793	170	95

the exchange of copper magnet coils for the original silver coils. Some development activities were started in the beta tanks in an effort to improve mercury collections and to establish quick startup techniques.

Radioactive

Two of the eight available separators in the alpha-contained area are being used to enrich ^{230}Th from a limited feed that contains 9 to 10% ^{230}Th. This separation, also on a 5-day around-the-clock basis, is being made to recover ~2 g of ~90% ^{230}Th.

Future separations in the contained area will include the recovery of 2 to 3 mg of >99% ^{246}Cm in a second-pass separation, ~500 g of ^{235}U enriched to >99%, and ~35 g of plutonium enriched to >95%.

GE ANNOUNCES AVAILABILITY OF ^{99}Mo

Fission product ^{99}Mo is now available from General Electric Company, Vallecitos Nuclear Center, Pleasanton, Calif. The isotope, which is >99.99% pure and has a specific activity of >5 thousand Ci/g, is the parent of ^{99m}Tc, which is used in medicine to detect lesions in the brain, kidneys, lungs, liver, and other organs. The ^{99}Mo was introduced at a price of $225 per curie, precalibrated for 4 days from the date of scheduled delivery, with a packaging charge of $100.

NEW ISOTOPE SHIPPING CONTAINER

Aeroquip Corporation/Marman Division, 11214 Exposition Boulevard, Los Angeles, Calif. 90064, offers a new isotope shipping container that incorporates a 1-in. Conoseal Joint closure. The new capsule eliminates the necessity for remote welding, permits clean assembly, and is inexpensive enough to be discarded after one use.

LOCKHEED TO CLOSE NUCLEAR LABORATORY

Lockheed-Georgia is closing, at least temporarily, its nuclear laboratory in Dawsonville, Ga. This laboratory, acquired from the U. S. Government in 1965, opened in 1957 for research on nuclear-powered aircraft and was later used for the study of effects of radiation on equipment, for nuclear equipment development, and for wood-irradiation research.

CORNELL COURSE IN RADIATION TECHNIQUES IN ANIMAL SCIENCES

A training course on advanced techniques involving radioisotopes and radiation in animal science and veterinary medicine was sponsored at Cornell University in Ithaca, N. Y., by the International Atomic Energy Agency and the Food and Agriculture Organization. Twenty scientists and educators from 19 countries attended the 6-week session from July 20 through Sept. 4, 1970. The U. S. Atomic Energy Commission assisted in making arrangements for the course.

Professor C. L. Comar, Head of Physical Biology and Director of the Laboratory of Radiation Biology and a pioneer in such techniques [*Isotopes and Radiation Technology*, 4(1)], was director of the course and responsible for its organization and administration. He also lectured on principles and practices of radioisotope usage in biological research. This training course was the ninth sponsored by the FAO–IAEA in the United States for foreign students.

Directory of High-Energy Radiotherapy Centres, 1970 ed., IAEA, Vienna, 1970 (203 pp., $5.00).

Supplementary Keywords: *medicine; therapy; accelerator; worldwide; cobalt-60; cesium-137.*

The second edition of the *Directory* (first edition in 1968) lists, by city, 1670 centers in some 80 countries where radioisotope, both ^{60}Co and ^{137}Cs, and other high-energy teletherapy equipment (e.g., betatrons, linear accelerators, and Van de Graaff machines) is installed. Besides such information as address, energy of source, dose rate, model and manufacturer of equipment, and personnel employed, detailed tables are given showing distribution of centers by country, number of units installed per year, and other appropriate breakdowns of data.

The book should prove useful for anyone doing teletherapy work. (MG)

INCREASED AVAILABILITY OF BETA-EMITTING NUCLIDES

General Electric's new complex for processing beta-emitting nuclides increases the capacity for producing ^{14}C, ^{32}P, ^{35}S, ^{36}Cl, ^{45}Ca, and ^{63}Ni. Xenon-133, produced in a separate facility, will be available routinely in 1971.

XUM

AEC Activities

AEC LABORATORY DEVELOPS NUCLEAR PROBE TO SPOT MINERALS ON OCEAN FLOOR

A neutron probe, based on ^{252}Cf, for detection of minerals on the ocean floor has been successfully demonstrated by scientists at the AEC's Pacific Northwest Laboratory at Richland, Wash. The undersea probe can determine gold, silver, copper, manganese, and some 25 other elements in quantities as low as 1 oz/ton in 3 to 5 min. The device is designed to operate from either a surface ship or a submersible vehicle. The new technology uses ultralow-level and rapid neutron activation analysis. The ^{252}Cf emits neutrons which, when absorbed by the elements in question, induce a gamma radiation that is proportional to the amount of element present.

In the initial test, 200-lb mineral samples containing gold, silver, copper, and manganese were placed on the ocean bottom at Sequim Bay, Wash. The elements were detected and their amounts measured with a probe containing 0.2 mg of ^{252}Cf. The californium source was in a sealed stainless-steel cylinder approximately 0.5 in. diameter and 3 in. long, located at the end of the probe. A 1- or 2-min exposure of an area a few inches in diameter on the ocean floor is required, followed by a similar counting period with the detector. There is no environmental problem—the residual radioactivity in the ocean floor is nondetectable several hours after the irradiation.

Battelle–Northwest's research and development program calls for the development of a working prototype instrument that can be used for mapping minerals at depths of a thousand feet.

^{252}Cf INFORMATION CENTER

A ^{252}Cf information center has been established at the AEC's Savannah River Plant. The growing number of inquiries about the ^{252}Cf market-evaluation program, as well as technical questions about ^{252}Cf, have made it necessary to centralize and make readily available such information. A current bibliography of published literature on ^{252}Cf will be maintained. Questions will be directed to appropriate groups for answers.

Information regarding participation in the market-evaluation program, copies of the brochure and progress reports, and information and answers to questions about ^{252}Cf may be obtained by telephoning 803-824-6331, Ext. C-252, or writing to

Manager
Savannah River Operations Office
U. S. Atomic Energy Commission
Post Office Box A
Aiken, S. C. 29801

FIRST SPACE ATOMIC BATTERY TO BEGIN TENTH YEAR OF OPERATION

The first space atomic battery, developed by the AEC, is heading into its tenth year in orbit. The grapefruit-size radioisotope thermoelectric generator, SNAP-3A, was launched June 29, 1961, from Cape Kennedy on a navigational satellite, and the generator has already operated 4 years beyond its 5-year design life. The SNAP-3A was designed to convert the heat given off by the ^{238}Pu fuel directly into 2.7 W of electricity. The prime contractor was the Martin Company, recently bought by Teledyne, Inc.

Development of the SNAP series has continued, with SNAP-27 placed on the moon in 1969 [see *Isotopes and Radiation Technology*, 7(4): 443-447; 449-451 (Summer 1970); and p. 261 in this issue].

AEC EXHIBITS

The Life Science Radiation Laboratory, a traveling exhibit featuring live demonstrations of the use of radiation in research, began showings on July 17, 1970, at the Columbus, Ohio, Center of Science and Industry. The exhibit uses live animals, insects, fish, and growing plants as well as inorganic materials to illustrate beneficial uses of radiation in biology, agriculture, and medicine. Demonstration experiments include exposing garden seeds, plants, and inorganic materials to radiation, and using radioisotopes as tracers to follow activities of animals and insects. The spectator and the demonstrator study the results together.

The exhibit Your Stake in the Atom, designed principally for state and local fairs, began its tenth season on the road on July 29, 1970, at the Central Wyoming Fair and Rodeo in Casper. The 4-day Casper showing was the first of eight appearances at fairs in

XUM

five western states, with the season continuing through early November 1970. The exhibit consists of 100 linear feet of colorful and animated display panels explaining the nation's nuclear energy research and development programs. Housed in a geodesic "Exhibidome," 50 ft in diameter and 25 ft high, the exhibit is manned by a specially trained science teacher–demonstrator and includes a demonstration of remote-controlled mechanical hands.

Both exhibits are operated for the AEC by Oak Ridge Associated Universities. Information on them may be obtained from the Information and Exhibits Division, Oak Ridge Associated Universities, P. O. Box 117, Oak Ridge, Tenn. 37830.

DIVISION OF ISOTOPES DEVELOPMENT DESCRIBES PROGRESS ON RESEARCH AND DEVELOPMENT PROJECTS IN 1970

The progress made in research and development projects sponsored by the USAEC's Division of Isotopes Development (DID) is covered in a recent report published by the AEC. This 165-page document, TID-4066,* describes DID-sponsored work during 1970, both at AEC laboratories and plants and at various industrial and academic facilities.

The goals of the major program areas funded by the Division and the number of projects under each are as follows:

Radioisotope Production and Materials to improve methods for the production of radionuclides—47 projects.

Radiation Analysis and Control to develop basic technology and instrumentation for detection and measurement of radioisotopes and to apply the technology to problems of current interest—23 projects.

Process Radiation to develop methods for the production of chemicals and other materials using large sources of radiation and to develop efficient, safe radiation sources for process radiation—20 projects.

Radiation Preservation of Foods to develop a low-dose radiation processing method to extend marketing times and reduce spoilage of selected foods—13 projects.

Environmental and Ocean Sciences to develop radioisotope techniques to aid in environmental problems such as pollution and water management and to assist in the exploration and economic development of the oceans—12 projects.

Thermal Applications to develop applications using the thermal energy generated by radioisotopic decay as a heat source, or for conversion to mechanical power—10 projects.

Analysis and Evaluation to collect and disseminate worldwide information on the production and use of radioisotopes and to conduct analytical studies to evaluate objectives and outputs of proposed Division projects—1 project.

Among the projects dealt with in this report is the development of new methods for the production of isotopes and some of their applications in medicine, ocean exploring, space travel, heart-assist devices, recovery of potable water from human wastes, detection of art forgeries, and preparation of concrete–polymer materials.

The report also reviews such environmental studies as tracing of sulfur dioxide in stack gases by the ratio of the stable isotopes ^{35}S to ^{34}S, analysis of pollutants in auto exhaust, and sand-tracing to help solve problems of coastline maintenance.

The report is for sale for $3.00 by the National Technical Information Service, 5285 Port Royal Rd., Springfield, Va. 22151. A limited number of copies are available free from the U. S. Atomic Energy Commission, Division of Isotopes Development, Washington, D. C. 20545.

AEC REVISES INSPECTION AND MAINTENANCE FOR RADIOGRAPHY EQUIPMENT

Supplementary Keywords: *regulation; safety.*

The AEC plans a change in its regulations to require licensees doing radiographic work to have programs for the inspection and maintenance of radiography equipment. Under a proposed amendment to Part 34, CFR, a licensee authorized to use sealed radioactive sources in radiography would be required to have an inspection and maintenance program for the radiographic exposure devices and storage containers that he uses. The licensee could either incorporate the recommendations of the equipment manufacturer into his program or independently prepare instructions for consideration by the Commission. The licensee's program for inspection and maintenance of radiography equipment would be subject to periodic inspection by the AEC's Division of Compliance.

*This report is the fourth published by DID [the other three are TID-24349 (1967); TID-24823 (1968); and TID-25372 (1969)].

XUM

The proposed amendment is intended to reduce the number of radiation exposures attributable to improperly maintained equipment.

Information on these revisions and the date on which they become effective may be obtained from the Secretary, U. S. Atomic Energy Commission, Washington, D. C. 20545, Attention: Chief, Public Proceedings Branch.

CONTRACTS AWARDED

Following are some of the recent contract awards and renewals by the Division of Isotopes Development:

Gulf Radiation Technology, a Division of Gulf Energy & Environmental Systems, Inc., P. O. Box 608, San Diego, Calif. 92112: Development of Nuclear Analytical Techniques for Oil Slick Identification.

University of Rhode Island, Kingston, R. I. 02881: Radioisotope Sediment Density Gage for the Deep Ocean Sediment Probe.

U. S. Department of Agriculture, Pacific Southwest Forest and Range Experiment Station, Berkeley, Calif. 94701: Nuclear Techniques in Soils Hydrology, Snow Gaging, and Related Applications.

Tyco Laboratories, Waltham, Mass. 02154: Cadmium Telluride Crystal Growth and Nuclear Detector Device Development.

Bureau of Reclamation, U. S. Department of the Interior, Denver, Colo. 80225: Development of Concrete–Polymer Materials.

University of Maryland, College Park, Md. 20742: Radiation-Induced Chain Reactions in Heterogeneous Systems.

AEC ADVISORY COMMITTEE

Three new members have been named to AEC's Advisory Committee on Isotopes and Radiation Development: Vincent P. Guinn, chemistry professor at University of California at Irvine; Bernard Manowitz, head of the Brookhaven National Laboratory Radiation Division; and Edwin A. Wiggin, technical projects manager for the Atomic Industrial Forum. Ira L. Morgan, director of the University of Texas Center for Nuclear Studies, has been appointed chairman.

General

FOOD IRRADIATION IN CANADA

Supplementary Keywords: *food preservation; industry, food; review, popular; agriculture.*

The status of the food-irradiation program in Canada was reviewed recently for *Nuclear Canada.** Canada has approved the use of radiation on three foods, but no private firm in the country is operating an irradiator for this purpose. An abortive attempt to sell irradiated potatoes on a commercial basis was a setback.† In Canada, as in the United States, the government is emphasizing high-priority projects at the expense of exploratory studies.

The top-priority studies supported by Atomic Energy of Canada Limited (AECL) have been the radurization of fresh fish and eviscerated poultry. Petition data will be supplemented with data from the Netherlands for irradiated chicken and from the United Kingdom for irradiated fish. Chickens are irradiated to 0.7 Mrad. The fish—haddock—will be given doses of 200 krads, although research in Canada has shown that high-quality fillets have an extended shelf life after a dose of only 100 krads.

The AECL mobile irradiator was used in 1968 to treat scallops, plaice, and yellow flounder. A dose of 225 krads increased the shelf-life of scallops by 8 days. The optimum dose for plaice and yellow flounder is evidently between 75 and 150 krads.

Radurization of round steak has shown that 500 krads provides a shelf life of 3 weeks at 40°F; controls were spoiled at 10 days. However, flavor changes were apparent in the irradiated meat; a lower dose will be used, with less gain in shelf life. Studies on the rehydration of irradiated freeze-dried beef have been completed. The University of British Columbia is studying the effects of pasteurizing doses of radiation on protein and lipid fractions in red meat.

*Food Irradiation, *Nuclear Canada*, 9(7): 12-14 (July–August 1970).

†First Commercial Food Irradiator Bankrupted by Crop Failure, *Isotopes and Radiation Technology*, 4(2): 203 (Winter 1966–1967).

Salmonella studies have shown that a dose of 500 krads will eliminate this pathogen from ground beef without affecting the vitamin A content. The same proved true of *Staphylococcus aureus* in cured meats. Salmonella research at the University of Manitoba showed that a dose of 700 krads will reduce this pathogen adequately in a frozen egg substrate. The University of Alberta showed that a dose of more than 400 krads is needed to control salmonella in skim-milk powder, but this dose causes development of an off-flavor.

Other products being studied include mushrooms and strawberries. A petition has been submitted to the government to approve mushrooms; it includes data from the Netherlands, which has cleared the use of radiation to retard cap opening of mushrooms. Because of the short growing season in Canada, strawberries do not have the high priority on obtaining clearance there that they do in the United States. Other studies are under way on blueberries, cherries, and cranberries. Doses used are up to 500 krads. Apple juice has been irradiated up to 600 krads with no change in *p*H and acidity, but there are changes in pectin and sugars.

Related programs using radiation in agriculture involve the use of low doses on seeds to stimulate growth and the sterilization of diets for laboratory animals. Crops studied included sweet corn, tomato, lettuce, egg plant, onion, cucumber, strawberry, rutabaga, green beans, field corn, barley, flax, spring wheat, durum wheat, oats, and grasses. Encouraging results have been obtained with cucumbers and strawberries. In addition to laboratory-animal diets, poultry feed has been treated successfully with 1 Mrad to reduce salmonella infection. (FEM)

AMERSHAM RECEIVES QUEEN'S AWARD

For the second time in 3 years, the Queen's Award to Industry has been made to the U. K. Atomic Energy Authority. It was awarded to the Authority's Radiochemical Centre, Amersham, for technological innovation in the production of the radioisotope ^{14}C and its compounds. In 1967 the Centre received the Queen's Award for export achievement and for technological innovation in the production for sale of radioisotopes for use in industry.

^{60}Co SEWAGE-TREATMENT PLANT INSTALLED

A sewage-treatment plant, designed and constructed by Energy Systems, Inc., of Melbourne, Fla., has been installed at a campground near Palmdale, Fla. It is claimed that the gamma radiation from ^{60}Co degrades up to 95% of the detergents present, whether biodegradable or not, and algae growth is inhibited. There is no residual activity, and operation, since startup in March 1970, is reported as having been economically competitive with conventional sewage-treatment processes. The ^{60}Co source and accessory equipment can be added to existing treatment plants.

NEW TECHNIQUE FOR NONDESTRUCTIVE DETERMINATION OF PROTEIN QUALITY

Supplementary Keywords: *biochemistry; nutrition; X-ray machine; agriculture; measurement, other.*

A new technique for determining the quality of protein—for example, that in cereal grains—is announced by the Lawrence Radiation Laboratory (LRL) at Berkeley, Calif., operated by the University of California (UC) for the AEC. Melvin P. Klein, physicist at LRL, and L. N. Kramer, graduate student in chemistry at UC, developed the method. Proteins are composed of more then 25 different amino acids, some of which are "essential," i.e., they cannot be synthesized by the human body. The new method identifies the individual acids, while previous methods have determined only the total protein.

The instrument used in the new procedure is an X-ray photoelectron spectrometer. Cereal grains under study are exposed to the radiation from an X-ray source in the instrument. As a result, electrons are emitted with energy patterns typical for each of a number of amino acids. Seed samples do not need to be destroyed. A portion of a seed can be tested, and, if the sample is promising, the remainder of the seed can be planted and will grow. In this way mutants can be selected on a scientific rather than a trial-and-error basis, and faster progress in developing the desirable grains may result. It has been estimated that a 10 to 20% increase in quantity and quality of proteins in grains could have an enormous impact on world food supplies without changing agricultural or dietary habits.

TOUR GROUP OF LATIN-AMERICAN AND ASIAN SCIENTISTS STUDIES U. S. INDUSTRIAL USES OF RADIOISOTOPES

Eighteen scientists from 16 Latin-American and Asian nations toured the United States and Canada from Aug. 10 to Sept. 18, 1970, to study the applica-

XUM

tions of radioisotopes and radiation techniques in industry. The tour was sponsored by the International Atomic Energy Agency.

The U. S. Atomic Energy Commission conducted the U. S. portion of the tour, which included stops at 37 private manufacturing plants and government laboratories. Tour participants are engineers or scientists engaged in planning, developing, or applying radioisotopes and radiation techniques in their own countries.

Study Tour Group at Oak Ridge National Laboratory's Isotopes Development Center.

Participants:

(1) Hong-Chien Yuan, IAEA, Vienna (tour guide)
(2) Soetarjo Soepadi, Bandung Reactor Center, Indonesia
(3) Krisadang Chirasanta, Thai Office of Atomic Energy for Peace, Bangkok
(4) Mohammad Samdani, Pakistan Atomic Energy Commission, Atomic Energy Center, Dacca
(5) Poh Lin, Singapore Institute of Standards and Research
(6) Jung Yeh, National Tsing Hua University, China
(7) Arthur Rajaratnam, University of Singapore
(8) Freddie Orbe, National Polytechnic School of Nuclear Science Institute, Quito, Ecuador.
(9) Virul Mangclaviraj, Thai Office of Atomic Energy for Peace, Bangkok
(10) Kyung Yang, Korean Atomic Energy Research Institute, Seoul
(11) Nguyen Khang, Dolat Nuclear Research Center, Vietnam
(12) Holger Valqui, National Engineering University, Lima, Peru
(13) Carlos Castagnet, National Nuclear Energy Commission of Argentina
(14) Andres Lalanne, University of Uruguay, Montevideo
(15) Carlos Garcia-Moreno, National Nuclear Energy Commission of Mexico
(16) Noel Carazo, Guatemala National Institute for Nuclear Energy
(17) Angelo Maestrini, National Nuclear Energy Commission of Brazil
(18) Alberto Campos, Philippine Atomic Energy Commission
(19) Shri Krishnamurthy, Bhabha Atomic Research Centre, Bombay, India

RECENT REPORTS OF DIVISION OF ISOTOPES DEVELOPMENT CONTRACTORS

K. A. Abood, J. P. Lawler, M. D. Disco, Utility of Radioisotope Methodology in Estuary Pollution Control Studies. Part I: Evaluation of the Use of Radioisotopes and Fluorescent Dyes for Determining Longitudinal Dispersion Coefficient in Estuaries, USAEC Report NYO-3961-1, Quirk, Lawler & Matusky Engineers, August 1969.

E. M. Ahmed, R. A. Dennison, and M. S. Merkley, Effects of Low Level Irradiation upon the Preservation of Food Products, USAEC Report ORO-675, University of Florida, April 1968.

E. M. Ahmed, R. A. Dennison, and M. S. Merkley, Effects of Low Level Irradiation upon the Preservation of Food Products, USAEC Report ORO-677, University of Florida, July 1969.

D. E. Bryan, V. P. Guinn, R. P. Hackleman, and H. R. Lukens, Development of Nuclear Analytical Techniques for Oil Slick Identification (Phase I), USAEC Report GA-9889, Gulf Radiation Technology, A Division of Gulf Energy & Environmental Systems, Inc., Jan. 21,1970.

H. K. Chow, R. F. Weise, and P. Flinn, Moessbauer Effect Spectrometry for Analysis of Iron Compounds, USAEC Report NSEC-4023-1, International Chemical and Nuclear Corporation, October 1969.

N. E. Davis and E. W. Johnson, Life Support II Program Final Report, USAEC Report MLM-1757, Mound Laboratory, A Subsidiary of Monsanto Company, Oct. 28, 1970.

D. B. Duane and C. W. Judge, Radioisotopic Sand Tracer Study, Point Conception, California. Preliminary Report on Accomplishments, July 1966–June 1968, Miscellaneous Paper No. 2-69, U. S. Army Coastal Engineering Research Center, May 1969.

J. T. Graikoski, S. DuCharme, M. Jackson, and S. Dudley, Preparatory Efficacy Studies for the Application of Ionizing Radiations to the Extension of the Refrigerated Storage of Freshwater Perch (*Perca flavescens*), Final Report, USAEC Report TID-25467, National Marine Fisheries Service, June 1, 1968.

R. L. Hansen and G. A. Teter, Use of Radioisotopes in Tracing Reservoir Leakage at Anchor Dam, USAEC Report TID-25396, U. S. Bureau of Reclamation, July 1970.

P. Harteck and S. Dondes, A Study of Improved Isotope-Excited Light Source Techniques, USAEC Report RPI-3816-4, Rensselaer Polytechnic Institute, January 1970.

C. Kim, Cobalt-60 Heat Source Demonstration Program. Phase I—Preliminary Analysis and Design Technical Report, USAEC Report WANL-543-1, Westinghouse Electric Corporation, Astronuclear Laboratory, January 1970.

C. N. Klahr and M. S. Cohen, Fabrication of Silicon Microcircuits by Neutron Transmutation Doping, Final Report, USAEC Report NYO-3124-3, Fundamental Methods Associates, Inc., Dec. 31, 1968.

J. A. Liuzzo, A. F. Novak, R. M. Grodner, and M. R. Ramachandra Rao, Radiation Pasteurization of Gulf Shellfish. I. Annual Report for the Period January 1, 1969, to December 31, 1969. II. Final Summary of the Total Program, USAEC Report ORO-676, Louisiana State University, February 1970.

E. C. Maxie, N. F. Sommer, and D. S. Brown, Radiation Technology in Conjunction with Postharvest Procedures as a Means of Extending the Shelf Life of Fruits and Vegetables, USAEC Report UCD-34-P-80-6, University of California, Davis, Jan. 30, 1968.

D. Miyauchi and F. Teeny, Application of Radiation-Pasteurization Processes to Pacific Coast Fishery Products, Annual Report, USAEC Report TID-25545, National Marine Fisheries Service, October 1970.

R. J. Pfeifer, Measurement of Sulfur Dioxide in Stack Gases. Demonstration Instrument—Design, Fabrication, and Test, USAEC Report NYO-3882-2, Industrial Nucleonics Corporation, May 28, 1970.

L. E. Preuss, C. Artman, and C. Bugenis, A Compilation of Beta-Excited X-Ray Spectra. Part III. ^{14}C, ^{3}H, ^{35}S, ^{89}Sr, ^{99}Tc, ^{185}W, ^{85}Kr, USAEC Report TID-22361 (Part 3), Edsel B. Ford Institute for Medical Research, Henry Ford Hospital, June 1970.

J. P. Scheiwe and D. E. Cressman, Development and Testing of Isotopic Shock-Wave Position Sensor, USAEC Report NYO-4071-1, Industrial Nucleonics Corporation, June 5, 1970.

J. C. Schuster and R. L. Hansen, Discharge Measurements Using Radioisotopes at Flatiron and Pole Hill Powerplants, USAEC Report TID-25395, U. S. Bureau of Reclamation, August 1970.

XUM

AEC Critical Review Series

THE ANALYSIS OF ELEMENTAL BORON

Morris W. Lerner, New Brunswick Laboratory
New Brunswick, New Jersey

November 1970

The importance of boron in nuclear technology and other fields has stimulated the development of new methods of analysis of elemental boron, boron carbide, and various boron mixtures. Also, enriched boron is of such monetary value that reliable methods of analysis are necessary.

In this compilation Dr. Lerner discusses the preparation and availability of assay and isotopic standards. Both chemical and physical methods for the determination of impurities, a heretofore completely neglected area, are considered. Detailed procedures are given for most determinations. Analysts concerned with characterizing boron products should find this review of the state of the art most helpful.

125 pages, 7 by 9¾ inches
Library of Congress Catalog Card: 74-607964

Available for $3.00 as TID-25190 from
National Technical Information Service
U. S. Department of Commerce
Springfield, Virginia 22151

"Instant" methods of analysis are provided in *The Analysis of Elemental Boron,* a practical book with a minimum of theory. Both the experienced analyst and the laboratory technician will find this book, which presents detailed analysis procedures, a valuable aid.

CONTENTS

Standards
Dissolution of elemental boron and boron carbide
Separations, losses, and contamination
Determination of boron
Isotopic analysis
Impurities in elemental boron
Determination of carbon, oxygen, nitrogen, and hydrogen
Determination of impurities
- Emission spectrograph
- Flame-emission and atomic-absorption spectroscope
- X-ray spectrograph
- Polarograph
- Spark-source mass spectrograph
- Neutron activation
- Spectrophotometer

Cooperative boron-analysis study
Subject index

NUCLEAR SCIENCE ABSTRACTS

The U. S. Atomic Energy Commission, Division of Technical Information, publishes *Nuclear Science Abstracts (NSA)*, a semimonthly journal containing abstracts of the literature of nuclear science and engineering.

NSA covers (1) research reports of the U. S. Atomic Energy Commission and its contractors; (2) research reports of government agencies, universities, and industrial research organizations on a worldwide basis; and (3) translations, patents, books, and articles appearing in technical and scientific journals.

Complete indexes covering subject, author, source, and report number are included in each issue. These indexes are cumulated and sold separately.

Availability

SALE *NSA* is available on subscription from the Superintendent of Documents, U. S. Government Printing Office, Washington, D. C. 20402, at $42.00 per year for the semimonthly abstract issues and $38.00 per year for the cumulated-index issues. Subscriptions are postpaid within the United States, Canada, Mexico, and all Central and South American countries, except Argentina, Brazil, Guyana, French Guiana, Surinam, and British Honduras. Subscribers in these Central and South American countries, and in all other countries throughout the world, should remit $52.50 per year for subscriptions to semimonthly abstract issues and $47.50 per year for the cumulated-index issues. The single-copy price for the abstract issues is $1.75 postpaid, with this exception: Add one-fourth of $1.75 for mailing to the countries to which the $52.50 subscription rate applies.

EXCHANGE *NSA* is also available on an exchange basis to universities, research institutions, industrial firms, and publishers of scientific information. Inquiries should be directed to the Division of Technical Information Extension, U. S. Atomic Energy Commission, P. O. Box 62, Oak Ridge, Tennessee 37830.

XUM

Subscription Information

Technical Progress Reviews may be purchased from Superintendent of Documents, U. S. Government Printing Office, Washington, D. C. 20402. *Nuclear Safety* at $3.50 per year (six issues) for each subscription or $0.60 per issue; *Reactor Technology* at $3.00 per year (four issues) for each subscription or $0.75 per issue; *Isotopes and Radiation Technology* at $2.50 per year (four issues) or $0.70 per issue.

Postage and Remittance

Postpaid within the United States, Canada, Mexico, and all Central and South American countries except Argentina, Brazil, Guyana, French Guiana, Surinam, and British Honduras. For these Central and South American countries and all other countries: add, for each annual subscription, $1.00 for *Nuclear Safety* and $0.75 for each of the other journals; for single issues, add one-fourth of the single-issue price. Payment should be by check, money order, or document coupons, and MUST accompany order. Remittances from foreign countries should be made by international money order or draft on an American bank payable to the Superintendent of Documents or by UNESCO book coupons.

XUM